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PRUSINSKI, D.

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THE PURPOSE OF THIS STUDY WAS TO DETERMINE THE APPLICABILITY OF ALUMINA IN REMOVING FLUORIDES FROM CARBON ADSORPTION TREATED NORTH BOUNDARY WATER. A LITERATURE SEARCH WAS MADE TO SURVEY ALL FLUORIDE REMOVAL METHODS. AS A RESULT OF THIS SEARCH, ALUMINA COLUMNS WERE FOUND TO BE THE MOST LIKELY CANDIDATE. TESTS WERE OUTLINED, SET-UP & RUN TO ANSWER QUESTIONS AS TO THE BEST VALUES REQUIRED FOR THE MOST EFFICIENT FLUORIDE REMOVAL.

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AT

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Supporting Program Under ITARMS 1.05.15

BY

Process Development and Evaluation Division

OF

THE CONTAMINATION CONTROL DIRECTORATE

Rocky Mountain Arsenal
Commerce City, Colorado 80022

November 1978

DENNIS M. PRUSINSKI
Chemical Engineer
Proc Devel. & Eval. Div.

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I would also like to thank the following people for their involvement in the beginning and finalization of the fluoride removal studies: Carl Loven, Ed Berry, Irwin Glassman and Connie Kniss.

TABLE OF CONTENTS

OUTLINE

Purpose: Determine applicability of alumina in removing fluorides from carbon adsorption treated north boundary water.

Methodology: Literature search made to survey all fluoride removal methods. Alumina columns found to be the most likely candidate as a result of the literature search. Important parameters were found to be:

1. pH,
2. Levels of other contaminates (especially organics),
3. Type of alumina used,
4. Shape of alumina used,
5. Level of fluoride concentration, and
6. Number of bed volumes (thus flow rate).

Tests were outlined, set-up and run to answer questions as to the best values required for the most efficient fluoride removal. The tests were:

1. Statistical survey of North Boundary dewatering wells which set the approximate chemical contamination levels,
2. Alumina column runs made on North Boundary water from the dewatering wells which tested flow rates and type of alumina for optimum values (since final system was not to adversely effect the water being discharged the effect pH was not tested; rather it was monitored),
3. Ruebel & Hager, Inc. subcontracted to study technical and economic compatibility of their system with the Calgon Plant adsorber effluent and the needs of RMA,
4. Isotherms were run on the different types of aluminas available to determine which alumina(s) had the greatest loading capacity, and
5. Aluminas selected from a combination of isotherm analysis and industrial recommendations were tested at Calgon plant.

STATISTICAL SURVEY TO DETERMINE LEVELS OF FLUORIDE AND OTHER CONTAMINATES IN NORTH BOUNDARY DEWATERING WELLS

Water samples of the North Boundary dewatering wells were collected over a six week period and the levels of contaminates found tested statistically to find mean and average levels for individual and composite dewatering wells plus two control wells. The result was fluoride levels were exceeding set standards with no reason for the high fluoride being attributable to natural causes.

ALUMINA COLUMNS SET-UP AND RAN USING WATER FROM THE DEWATERING WELLS WHICH WAS CARBON PRETREATED

Four alumina columns were set-up and tested at different flow rates to determine an optimum flow rate. Phased runs to find optimum pH and best type of alumina. The optimum flow rate was found but subsequent discussion revealed isotherm test would be more expeditious in determining the best type of alumina. It was also found that a pH adjustment would cause unnecessary complication in North Boundary water treatment. The alumina column test proved the technical feasibility but opened questions as to economic feasibility and industry's capability to handle the Calgon plant discharge. The questions posed were beyond the scope of PD&E efforts thus generating the need for a subcontract to answer these questions.

RUEBEL AND HAGER, INC. SUBCONTRACTED TO STUDY INDUSTRY'S TECHNICAL AND ECONOMIC FEASIBILITY ON FLUORIDE REMOVAL USING ALUMINA COLUMNS

Following award of contract, a technical group from Ruebel & Hager, Inc. brought out and set-up pilot plant equipment to test treatability of Calgon adsorber effluent and derive an estimate of the cost of a full scale fluoride removal process using alumina columns. Test run covered one run using "fresh" (activated) alumina followed by a second run which utilized regenerated alumina. Samples were collected at roughly 200 gallon intervals and analyzed for fluoride levels using three different methods. The cost of a full scale treatment scheme to reduce fluoride levels was determined by Ruebel & Hager, Inc. and the resulting report published.

ISOTHERM RUNS ON VARIOUS TYPES OF ALUMINAS TO DETERMINE THE HIGHEST LOADING CAPACITY

A series of isotherm tests were set-up and run to help narrow the number of different types to the aluminas most likely to succeed in alumina columns based on the loading capacity of each. In these tests measured amounts of

alumina were added to a fixed volume of Calgon plant adsorber effluent water. The results of the chemical analyses of fluoride levels were plotted using the Freundlich equation to find the ultimate loading capacity of each type of alumina. The ultimate loading capacities of each type could be directly compared and a selection made for the final column tests.

ALUMINAS WERE SELECTED FROM RESULTS OF ISOTHERM ANALYSIS COMBINED WITH CONSIDERATIONS OF INDUSTRIAL APPLICATIONS AND FINAL ALUMINA COLUMN TESTS

Of the several types of aluminas used for the isotherm tests, five types and shapes were selected with the number of aluminas further narrowed to two types. The narrowing to two types was made based on which aluminas of the five showing merit in the isotherm test had been used with any degree of success in industrial application to fluoride removal. The water samples collected during the test run were analyzed by both MALD and PD&E personnel. The results were sent to the Scientific Information & Applications Office center for a computer analysis and plotted using the Adsorption Column Analysis Program developed by Mr. R. Ruhge.

CONCLUSION AND RECOMMENDATIONS:

The statistical survey of the dewatering wells indicated consistantly high fluoride levels which exceeded set standards. This leads to the recommendation that the fluorides must be treated. The theory is fluorides could possibly be treated if the organic contaminates were significantly reduced. The need to test this theory was thus generated and simultaneously the need arose to find the important parameters and the prime levels for the most efficient fluoride removal and/or reduction. A literature search had indicated the use of alumina columns was best suited to treat the North Boundary aquifer water. Four one-inch columns were loaded with activated alumina and test runs made with varying flows. The alumina was

found to work very well on carbon pretreated North Boundary aquifer water. An optimum flow was found for one type of alumina at a set pH. Regeneration was made of the spent alumina and a second run made to exhaustion of the regenerated alumina. The results of the samples analyses were sent to SIAO center and an adsorption column computer program used to analyze the efficiency of the alumina at different flows and bed volumes (thus contact time was studied) versus fluoride levels. The conclusion reached from the computer program output was that alumina columns were effective in reducing fluoride levels.

A study to select the most favorable types of aluminas using the isotherm method was developed and run. The ALCOA F-1 Alumina was recommended due to its excellent industrial performance and the Kaiser A-201 Alumina Spheres was also recommended due to its high loading capacity for a final column run on the Calgon adsorber effluent. At the same time economic data and industrial capability to handle the Calgon plant adsorber discharge was an area of knowledge which could not be arrived at by a PD&E Section effort alone. This area required a contract to be let to provide the industrial viewpoint of cost items and technical feasibility. The Ruebel and Hager, Inc. report published as a result of a two week process plant experiment reflected an affirmative reply to the technical capability of their alumina column equipment to reduce the fluoride level significantly, with no adverse effects to the alumina occurring due to the other contaminates present in the Calgon plant adsorber discharge.

The final column run made on the Calgon plant adsorber discharge to determine the relative column efficiency for the two most promising aluminas revealed some very unexpected results. One result was that alumina pre-

soaked with Aluminum Sulphate performed better initially than the activated alumina which did not receive the pretreatment. Another result was that ALCOA F-1 Alumina out performed the Kaiser A-201 Alumina Spheres although the isotherms showed Kaiser A-201 to have a superior fluoride loading capacity. The other result was that the regenerated ALCOA F-1 Alumina performed better than the fresh activated ALCOA F-1 Alumina. It is, therefore, recommended that further work be accomplished to find the cause of these unexpected results. A field size plant may operate quite differently since "channelling" and other such size related problems are greatly reduced in larger columns.

INTRODUCTION

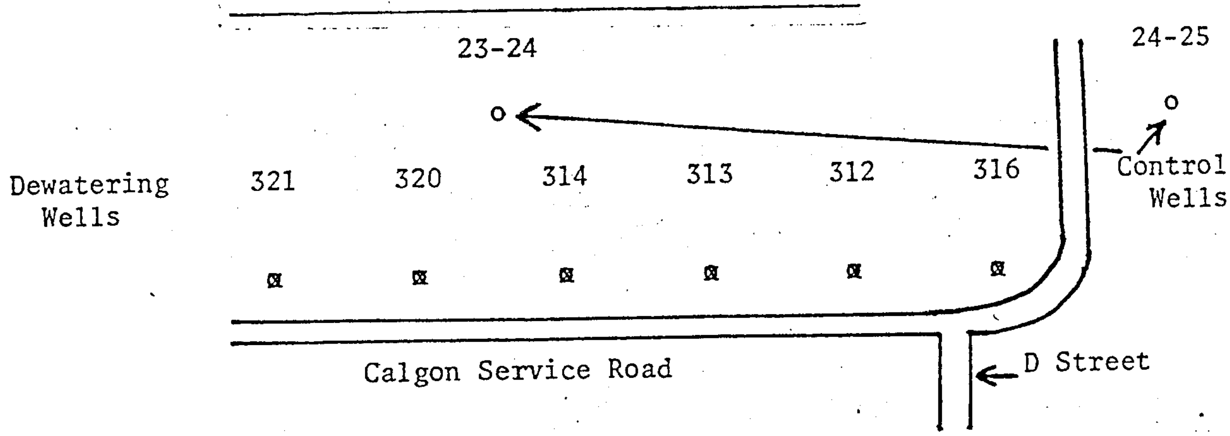
The following six sections are intended to provide the facts and reasoning that lead to the final section and resultant recommendations and conclusions. The material in these sections will provide an engineering base in fluoride removal technology development. Additionally, the information and answers arrived at emphasize where future effort and work is required.

STATISTICAL SURVEY OF NORTH BOUNDARY DEWATERING WELLS TO ASCERTAIN REPRESENTATIVE CONTAMINATE LEVELS

Water samples were collected from six dewatering wells which were to feed into the Calgon Pilot Treatment Plant, and water samples were also collected from two outlying control wells. The pattern of the referenced wells is given in Figure 1 below:

FIGURE 1

PATTERN OF DEWATERING AND CONTROL WELLS



A standard mean and standard deviation on the fluoride levels found in each well and for all the dewatering wells was performed. Minimum and maximum fluoride levels were used to set a range for the dewatering well fluoride levels. The two control wells, 23-24 and 24-25, gave some independent values for the statistical survey since these monitoring wells had had a long period of time (1 year or greater) to stabilize. Table 1 sets forth the results of the statistical survey of the contaminate levels of the North Boundary groundwater.

TABLE I

STATISTICS ON NORTH BOUNDARY DEWATERING AND CONTROL WELLS

Well #	$\bar{x}$ Fl*	σ^2 Fl**	σ Fl*	$\bar{x}$ pH	σ^2 pH	σ pH	Approximate Flows (gpm)
316	3.6	.135	.367	7.39	.0426	.2064	3
317	4.02	.406	.682	7.52	.0704	.2653	5
318	4.94	.150	.388	7.58	.0334	.1826	17
319	3.14	.062	.250	7.42	.0481	.2194	20
320	4.47	.228	.477	7.42	.0288	.1696	30
321	4.91	.104	.323	7.41	.0296	.172	32
Composite≠	4.20	.647	.804	7.45	N.G.	N.G.	107+

* - mg/l
** - $(mg/l)^2$
≠ - Includes two control wells which have had over one year to stabilize (23-24, 24-25)
\+ - Flow for control wells not included.

If the flows from the six dewatering wells are not considered, a distorted picture of the expected fluoride and pH levels would result. By using the flows as a weighing factor, w_f, and using the following formula, a better estimate of the expected fluoride and pH levels for the Calgon plant feed sump can be found:

(a) Fluoride level at feed sump to Calgon plant:

$$\sum w_f (Fl) = F_{tl}$$

Where; Fl = fluoride level (mg/l) at a particular dewatering well, w_f = flow of particular dewatering well divided by total flow of all dewatering wells and F_{tl} = fluoride level (mg/l) expected at Calgon plant feed sump.

(b) pH level expected at feed sump to Calgon plant:

$$\log_{10} \sum w_f (\exp pH_2) = pH_{tl}$$

Where; pH_2 = pH level at a particular dewatering well, w_f same as given in (a) and pH_{t1} = the pH level expected at Calgon plant feed sump.

The first calculation yields F_{t1} of 4.382 mg/l which exceeds the standard levels set for fluorides. The second calculation yields pH_{t1} of 7.442 which while slightly basic is not detrimental to carbon or alumina adsorption column schemes.

The problem of organics possibly causing a "cementation" of alumina was addressed by pretreating the dewatering well sample with activated carbon adsorption columns. In this way the levels of organics were not a significant factor in fluoride removal since the organic levels were greatly reduced by activated carbon. The completion of the Calgon carbon adsorption plant made the removal of fluorides by alumina column adsorption a realistic and possible idea. The next section deals with the set-up and use of alumina columns to remove and/or reduce the fluoride concentration levels of the activated carbon treated dewatering well sample. The analysis follows this experiment and gives the results and recommendations that were derived from the chemical analyses.

ALUMINA COLUMN TESTS TO DETERMINE FEASIBILITY AND IMPORTANT PARAMETER LIMITS FOR EFFICIENT FLUORIDE REMOVAL

The important parameters effecting fluoride removal using activated alumina were found by a literature review. These parameters were (1) pH, (2) type of alumina, (3) shape of alumina, (4) contact bed time (flow rate vs bed volume), (5) incoming F^- levels (<10 ppm) and (6) loss of adsorbative capacity due to other contaminates and/or fluoride being adsorbed on alumina. These same parameters applied to the regenerated alumina plus an additional parameter--efficiency of regenerative alumina versus activated alumina.

The first test run used a MCB crushed-spheres alumina with only the flows being altered in each of 4-one inch columns. Bed height (thus bed volume) was set for six feet. The pH level also was not changed from the natural level existing in the dewatering well sample. It was found that a 24 hour run was needed since the alumina columns would desorb when shut down over night on the 8 hour runs. The tabulized results are given in Table II, which relates fluoride levels at different sample heights (thus bed volumes) for each column which had a different flow rate. The sample group and total flow thru each column are given in Table III. The plot for the activated alumina run, which gives fluoride levels versus total number of bed volumes, is shown in Figures 2, 3, 4 and 5. Examination of the plots show (1) alumina becomes exhausted quicker with faster flow rates, and (2) fluoride levels are maintained at a lower level with increased bed volume. Also, it can be seen that the activated alumina can reduce the fluoride levels in the dewatering well sample to acceptable levels and thus satisfy the feasibility criterion.

The most efficient flow rate was found to lie between 100 ml/min and 300 ml/min. The spent alumina was regenerated in place with a second 24 hour run scheduled. The second run was set up so that the plot of the 200 ml/min flow rate column of the first test could be compared to the 200 ml/min flow rate column of the second run. The flows of the other columns were selected so that the most efficient flow rate could be closely bracketed. The plot derived from the data of this second test run is given in Figures 6, 7, 8 and 9. The results of the chemical analysis of the samples taken during the test run are given in Table IV. The total flow for each of the regenerated alumina columns at each sample group is given in Table V. Comparing Figures 2, 3, 4,

and 5 to 6, 7, 8 and 9, respectively, at the same sample points, it is readily seen that the regenerated alumina not only holds the fluoride levels longer (larger total number of bed volumes) but also compares well with the activated alumina (fluoride levels) in its spent region. The "spent" region is here defined as the area where fluoride levels approach those of the effluent and remain at fairly constant values.

TABLE II

FLUORIDE LEVELS AFTER TREATMENT OF DEWATERING WELLS WITH ACTIVATED ALUMINA

Sampling Group No.	Effluent	Fluoride Concentration ppm Column 1	Column 2	Column 3	Column 4	Sampling Point No.
1	3.6	3.08	3.0	2.61	2.02	1
		2.54	2.24	1.98	1.07	2
		2.0	1.49	1.11	.53	3
		1.84	1.54	1.02	.48	4
2	3.4	3.4	3.2	2.9	2.4	1
		2.8	2.5	2.1	1.2	2
		2.25	2.1	1.4	.62	3
		2.3	1.85	1.3	.58	4
3	3.5	3.05	3.0	3.05	3.0	1
		2.6	2.4	2.3	1.3	2
		2.5	2.4	1.7	.72	3
		2.6	2.2	1.7	.52	4
4	3.6	3.05	3.15	3.15	3.5	1
		2.8	2.9	2.6	1.6	2
		2.8	2.7	2.1	1.0	3
		2.8	2.25	2.1	.98	4
5	3.4	3.4	3.4	3.4	2.8	1
		3.2	3.05	2.6	1.8	2
		2.9	2.6	2.1	1.1	3
		2.6	2.6	1.85	1.05	4
6	Not Collected	3.3	3.3	3.2	2.8	1
		3.4	3.2	2.8	1.75	2
		2.6	2.8	2.3	1.20	3
		3.2	2.7	2.1	1.10	4
7	Not Collected	3.2	3.4	3.05	2.7	1
		3.3	3.2	2.7	1.8	2
		2.9	2.8	2.3	1.3	3
		2.8	2.7	2.25	1.25	4
8	Not Collected	3.3	3.3	3.3	2.8	1
		3.6	3.2	2.9	1.9	2
		3.05	3.05	2.3	1.45	3
		3.05	2.7	2.5	1.2	4

Sampling Group No.	Effluent	Fluoride Concentration ppm				Sampling Point No.
		Column 1	Column 2	Column 3	Column 4	
9	Not Collected	3.5 3.4 3.2 3.05	3.5 3.3 2.9 2.8	3.5 2.9 2.4 2.5	3.2 2.1 1.4 1.4	1 2 3 4
10	3.4	3.05 2.8 2.5 2.6	2.9 2.7 2.6 2.3	2.8 2.6 2.5 1.9	2.3 1.7 1.1 1.15	1 2 3 4

TABLE III

TOTAL FLOWS AT GIVEN ELAPSED TIME FOR EACH COLUMN ACTIVATED ALUMINA COLUMN RUN (BLDG 802)

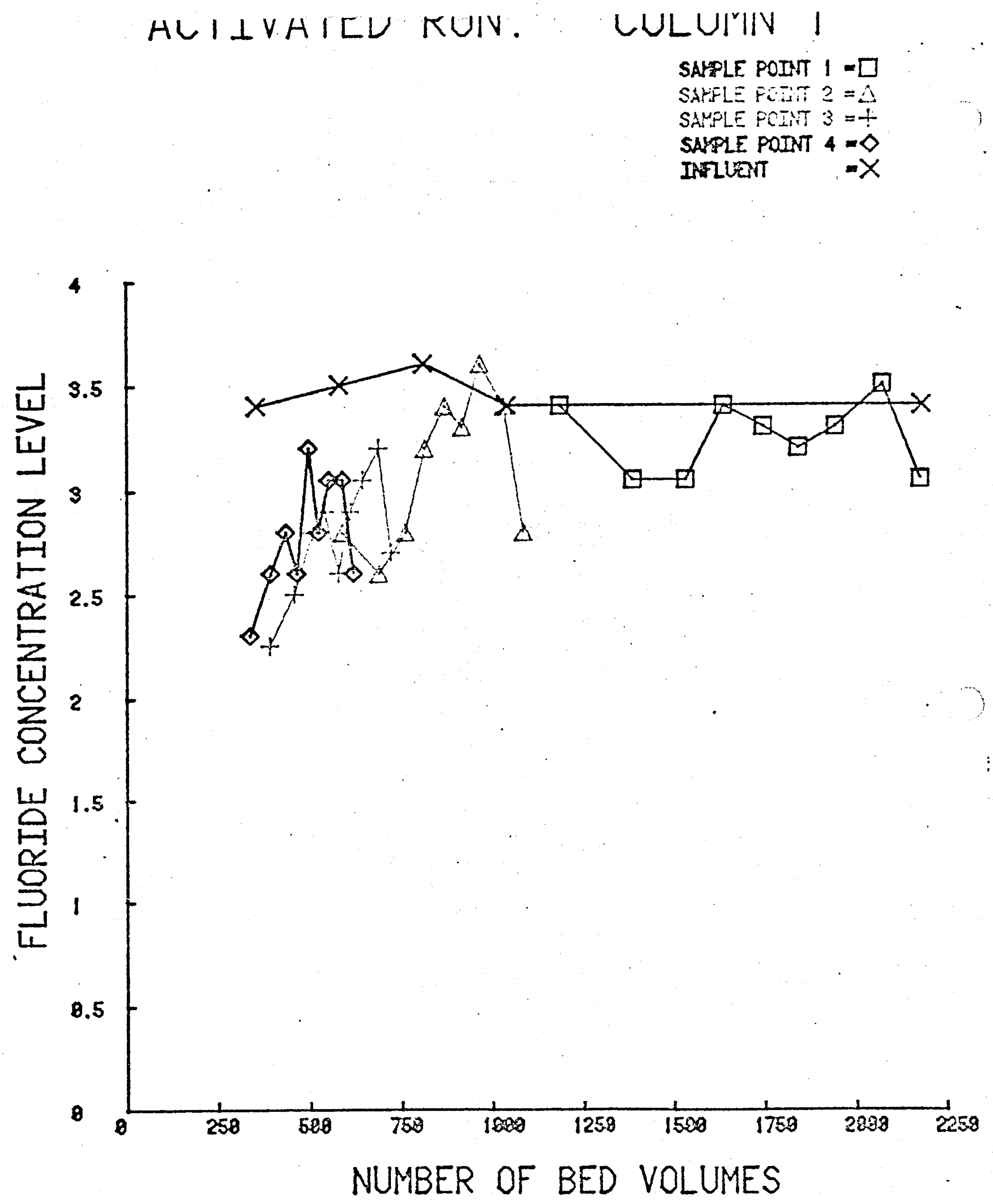
15 June 78 1500 Hours -- 16 June 78 1520 Hours

Column 1 400 ml/min
Column 2 300 ml/min
Column 3 200 ml/min
Column 4 100 ml/min

Activated Alumina

Sampling Group No.	Time	Elapsed Time (Mins.)	Column 1	Column 2	Column 3	Column 4
			Total Flows (ml)			
1	15 June *1710	130	52,000	39,000	26,000	13,000
2	1915	255	102,000	76,500	51,000	25,500
3	2315	495	198,000	148,500	99,000	49,500
4	0215	675	270,000	202,500	135,000	67,500
5	0420	800	320,000	240,000	160,000	80,000
6	0625	925	370,000	277,500	185,000	92,500
7	0810	1030	412,000	309,000	206,000	103,000
8	1020	1160	464,000	348,000	232,000	116,000
9	1255	1315	526,000	399,500	263,000	131,500
10	1510	1460	584,000	438,000	292,000	146,000

*Start: 1500 hours -- 15 June 78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SAMPLE POINT 2 =△
SAMPLE POINT 3 =+
SAMPLE POINT 4 =◇
INFLUENT =X
FLUORIDE CONCENTRATION LEVEL
4
3.5
3
2.5
2
1.5
1
0.5
0
0
250
500
750
1000
1250
1500
1750
2000
2250
NUMBER OF BED VOLUMES

FIGURE 2

ACTIVATED RUN: COLUMN 2

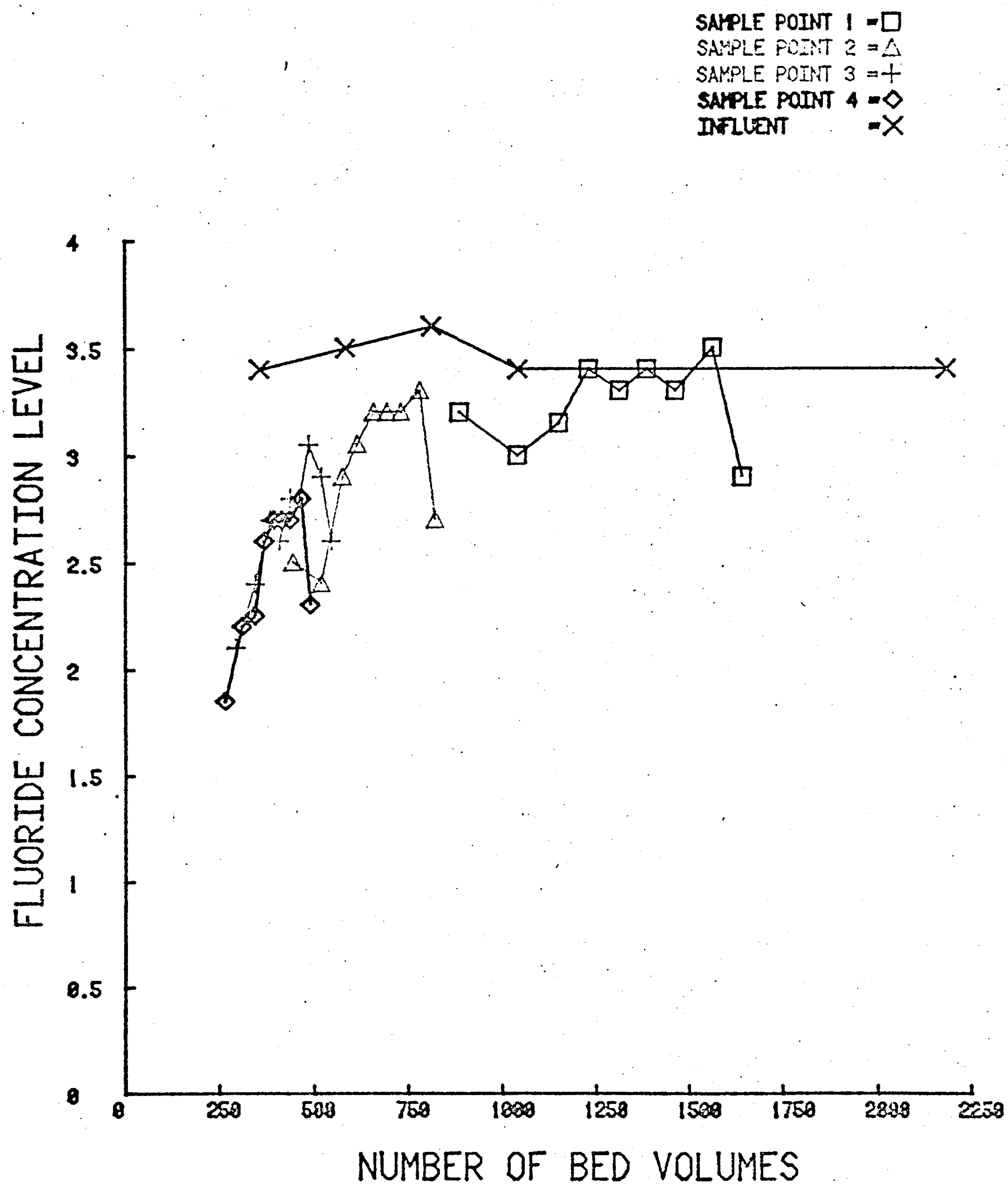
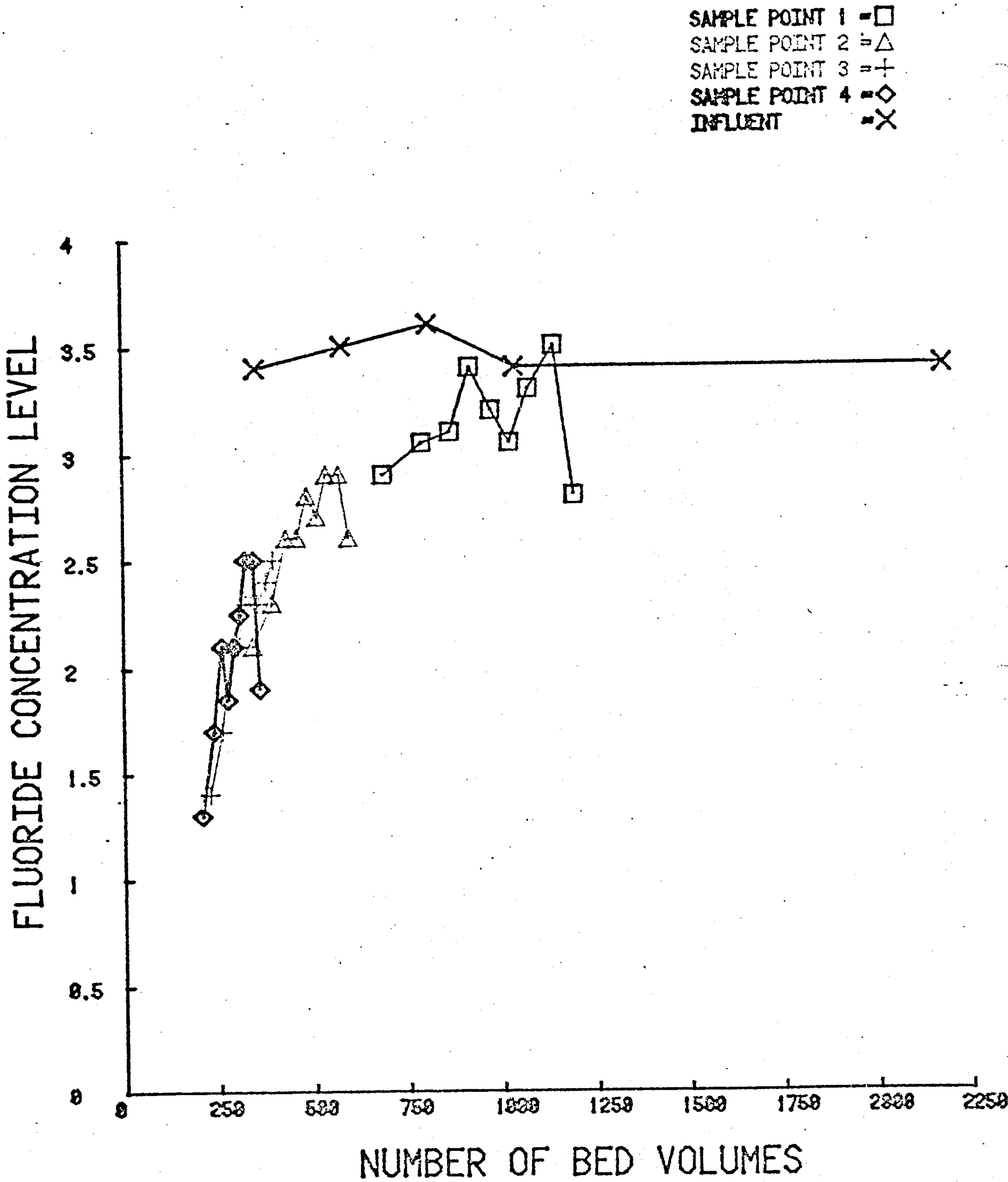


FIGURE 3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FLUORIDE CONCENTRATION LEVEL
4
3.5
3
2.5
2
1.5
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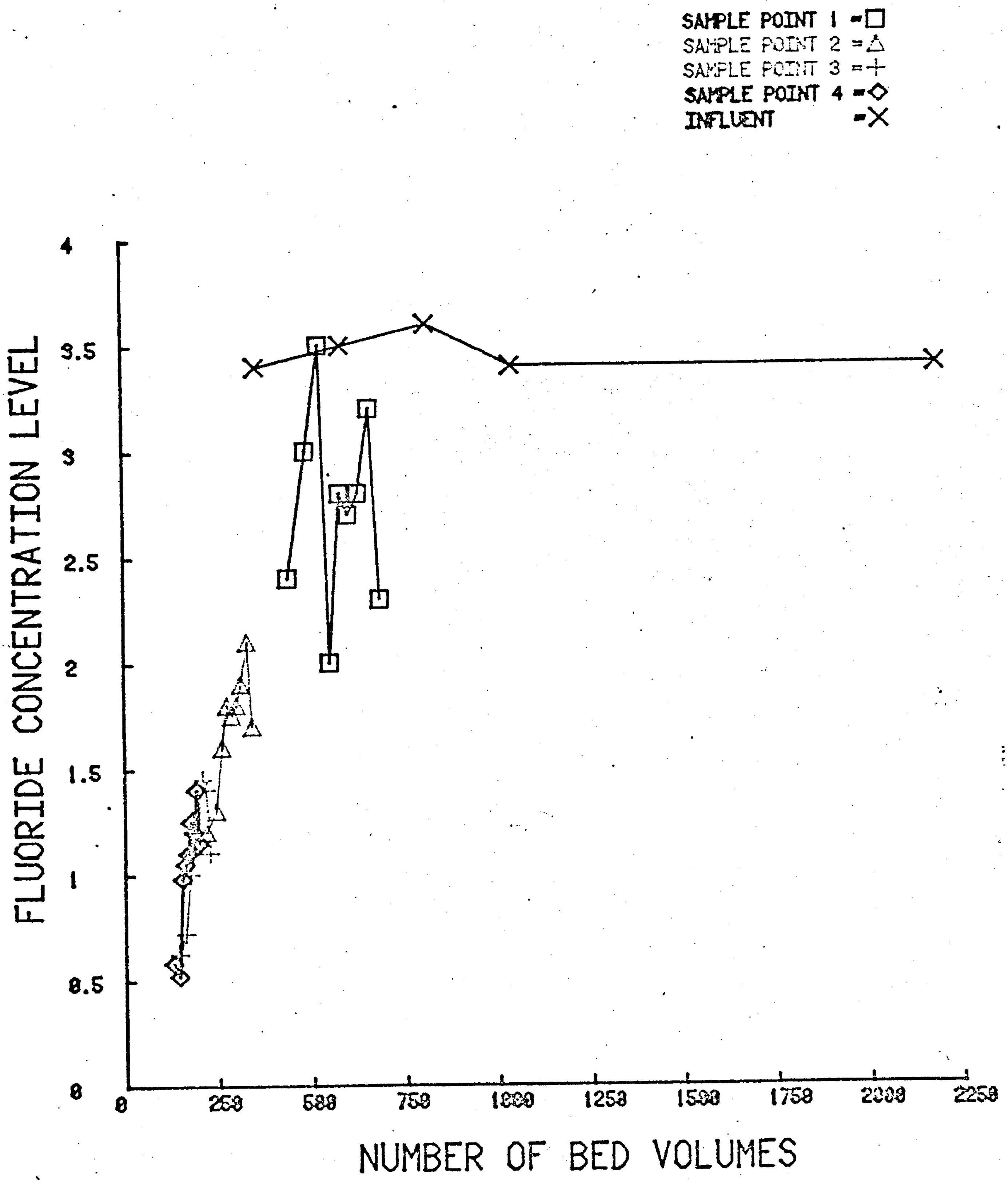
250
500
750
1000
1250
1500
1750
2000
2250
NUMBER OF BED VOLUMES

FIGURE 4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INFLUENT =X
FLUORIDE CONCENTRATION LEVEL
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3.5
3
2.5
2
1.5
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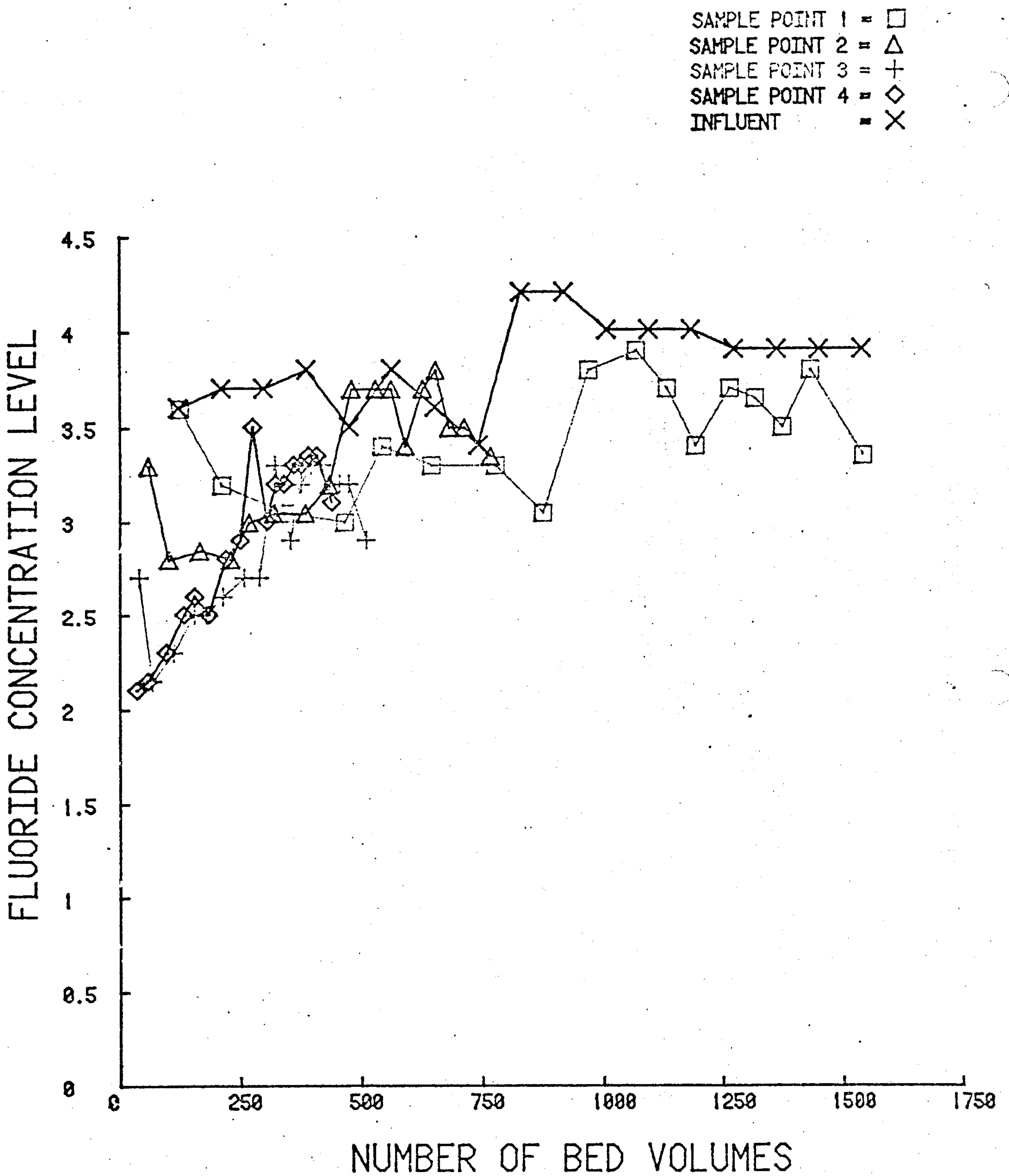
250
500
750
1000
1250
1500
1750
2000
2250
NUMBER OF BED VOLUMES

FIGURE 5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SAMPLE POINT 4 = ◇
INFLUENT = ×
FLUORIDE CONCENTRATION LEVEL
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
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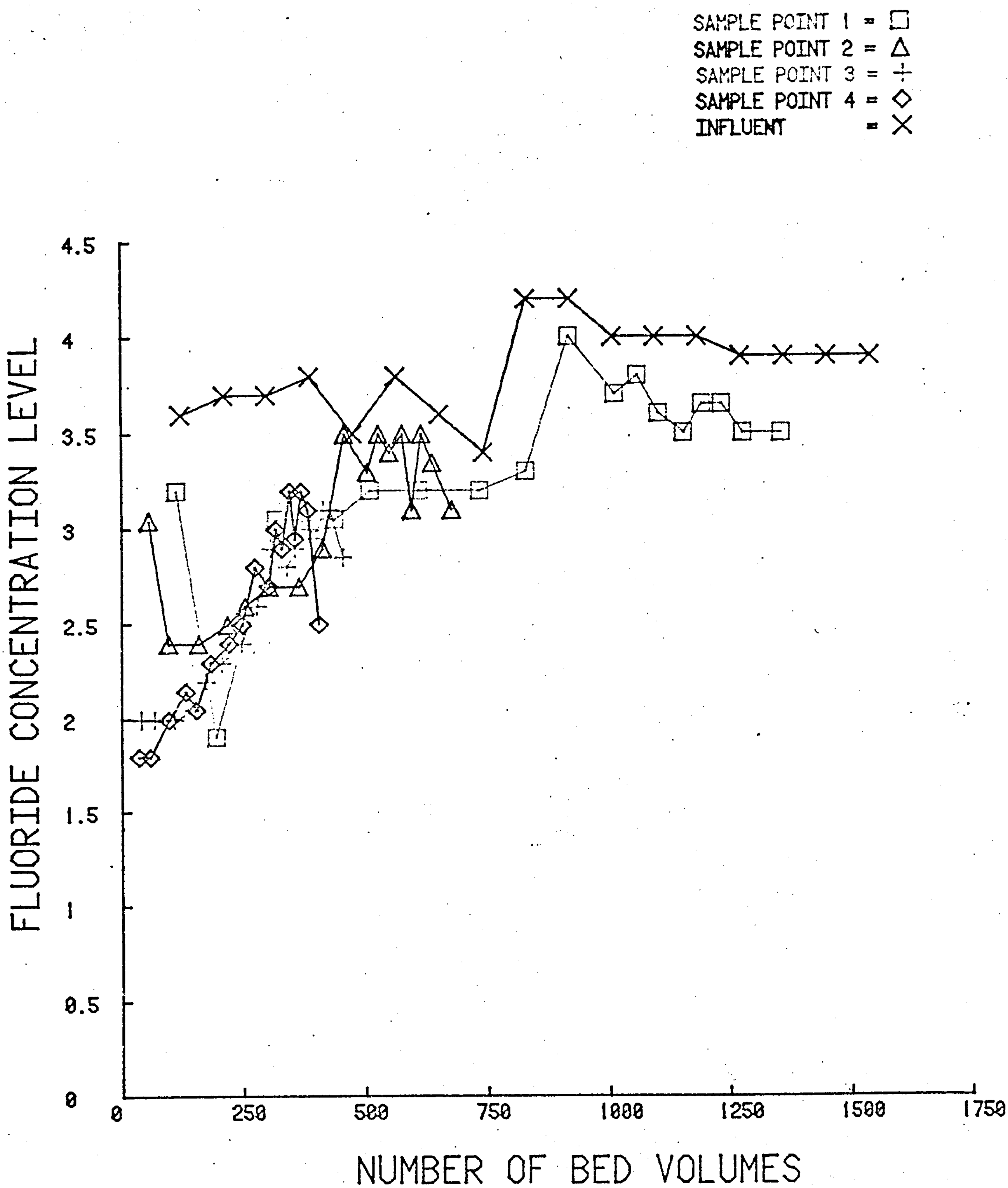
250
500
750
1000
1250
1500
1750
NUMBER OF BED VOLUMES

FIGURE 6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SAMPLE POINT 4 =
INFLUENT =
FLUORIDE CONCENTRATION LEVEL
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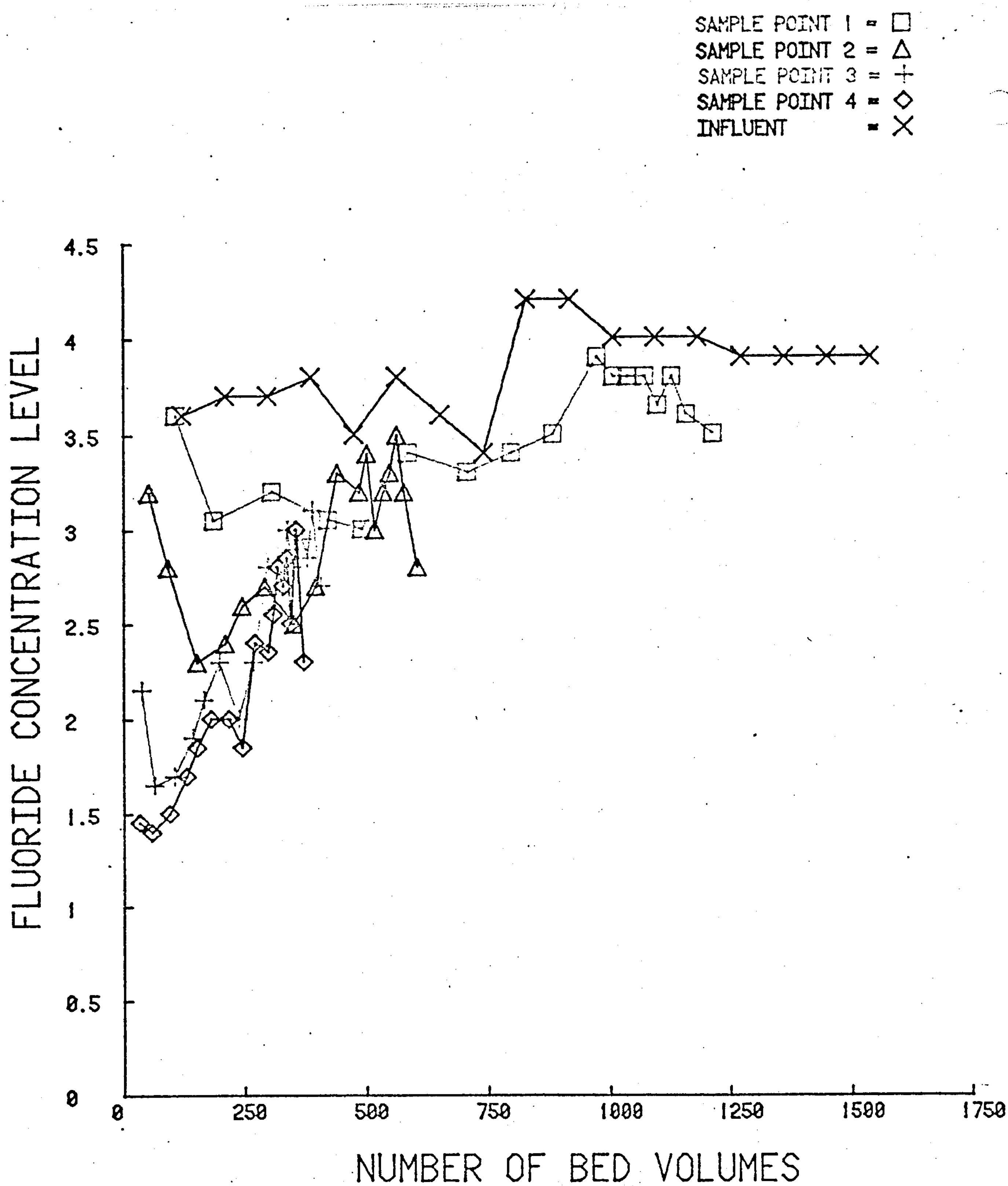
4
3.5
3
2.5
2
1.5
1
0.5
0
0
250
500
750
1000
1250
1500
1750
NUMBER OF BED VOLUMES

FIGURE 7



SAMPLE POINT 1 = □
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INFLUENT = ×
FLUORIDE CONCENTRATION LEVEL
4.5
4
3.5
3
2.5
2
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250
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750
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1250
1500
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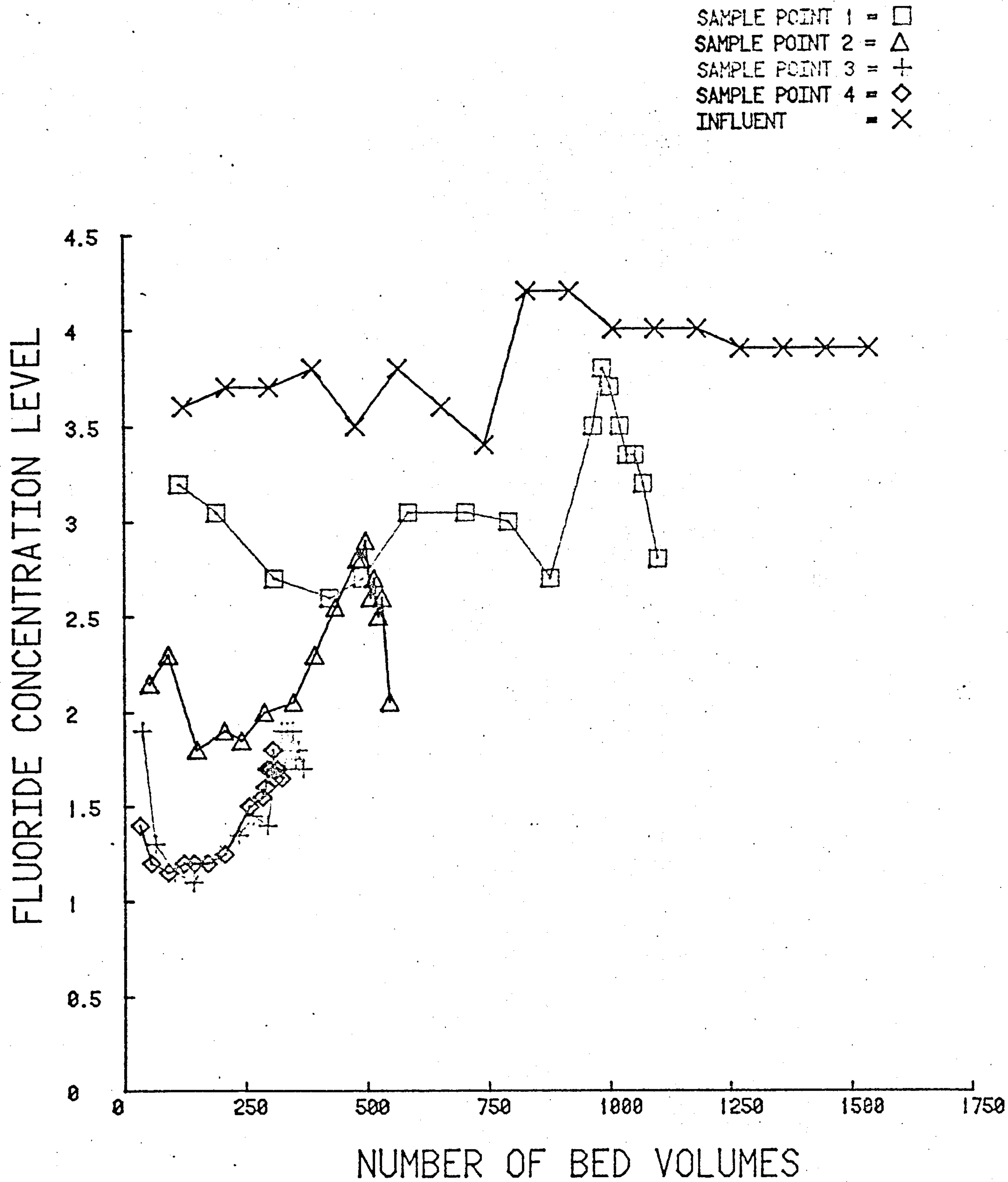
NUMBER OF BED VOLUMES

FIGURE 8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SAMPLE POINT 3 = +
SAMPLE POINT 4 = ◇
INFLUENT = ×
FLUORIDE CONCENTRATION LEVEL
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
250
500
750
1000
1250
1500
1750
NUMBER OF BED VOLUMES

FIGURE 9

TABLE IV

REGENERATED AND NEW FLOW IN FLUORIDE REMOVAL USING ALUMINA TEST IN BLDG 802

Sampling Group No.	Effluent	Fluoride Concentration ppm Column 1	Column 2	Column 3	Column 4	Sampling Point No.
1	3.6	3.6	3.2	3.6	3.2	1
		3.3	3.05	3.2	2.15	2
		2.70	2.0	2.15	1.9	3
		2.1	1.8	1.45	1.4	4
2	3.7	3.2	2.9	3.05	3.05	1
		2.8	2.4	2.8	2.3	2
		2.15	2.0	1.65	1.3	3
		2.15	1.8	1.4	1.2	4
3	3.7	3.05	3.05	3.2	2.7	1
		2.85	2.4	2.3	1.8	2
		2.3	2.0	1.7	1.15	3
		2.3	2.0	1.5	1.15	4
4	3.80	3.0	3.05	3.05	2.6	1
		2.8	2.5	2.4	1.9	2
		2.5	2.05	1.9	1.1	3
		2.5	2.15	1.7	1.2	4
5	3.5	3.4	3.2	3.0	2.7	1
		3.0	2.6	2.6	1.85	2
		2.5	2.2	2.1	1.2	3
		2.6	2.05	1.85	1.2	4
6	3.8	3.3	3.2	3.4	3.05	1
		3.05	2.7	2.7	2.0	2
		2.6	2.3	2.3	1.25	3
		2.5	2.3	2.0	1.20	4
7	3.6	3.3	3.2	3.3	3.05	1
		3.05	2.7	2.5	2.05	2
		2.7	2.4	2.0	1.35	3
		2.8	2.4	2.0	1.25	4
8	3.4	3.05	3.3	3.4	3.0	1
		3.20	2.4	2.7	2.3	2
		2.7	2.6	2.3	1.45	3
		2.9	2.5	1.85	1.30	4

Cont'd.

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TABLE V

TOTAL FLOWS FOR EACH REGENERATED ALUMINA RUN AT GIVEN ELAPSED TIME AT BLDG 802

Sampling Group No.	Time	Elapsed Time (Mins.)	Column 1	Column 2	Column 3	Column 4
			Total Flows (ml)			
1	20 Jul 0855	175	43,750	35,000	26,250	17,500
2	1015	225	56,250	45,000	33,750	22,500
3	1245	375	93,750	75,000	56,250	37,500
4	1455	505	126,250	101,000	75,750	50,500
5	1620	590	147,500	118,000	88,500	59,000
6	1820	710	177,500	142,000	106,500	71,000
7	2040	850	212,500	170,000	127,500	85,000
8	2240	970	242,500	194,000	145,500	97,000
9	21 Jul 0020	1070	267,500	214,000	160,500	107,000
10	0215	1185	296,250	237,000	177,750	118,500
11	0415	1305	326,250	261,000	195,750	130,500
12	0620	1430	357,500	286,000	214,500	143,000
13	0845	1575	393,750	315,000	236,250	157,500
105 14	1030	1680	417,375	330,250	244,650	161,175
225 15	1230	1800	444,375	348,750	254,250	165,875
335 16	1420	1910	469,125	365,250	263,050	169,225
560 17	1805	2135	519,750	399,000	281,050	177,100

* - Start: 0600 Hours 20 July 78

Flow Rates: Sampling Group 1-13		Flow Rates: Sampling Group 14-17	
Column 1	250 ml/min	Column 1	225 ml/min
Column 2	200 "	Column 2	150 "
Column 3	150 "	Column 3	80 "
Column 4	100 "	Column 4	35 "

FEASIBILITY STUDY

FOR THE

REMOVAL OF EXCESS FLUORIDE

FROM

ACTIVATED CARBON EFFLUENT

FOR

THE DEPARTMENT OF THE ARMY

ROCKY MOUNTAIN ARSENAL

(REF. #DAAA05-78-M-0914)

BY

Rubel and Hager, Inc.
4400 E. Broadway, Suite 710
Tucson, Arizona 85711

September 30, 1978

I N D E X

FEASIBILITY STUDY FOR THE REMOVAL OF EXCESS FLUORIDE FROM ACTIVATED CARBON EFFLUENT

I. Introduction

In accordance with a directive from the Colorado Department of Health, the reinjection water at the north boundary of the Rocky Mountain Arsenal will be subject to drinking water standards as established by the U. S. Environmental Protection Agency and the Colorado Department of Health (see Appendix H). In addition to organic limitations for which purpose the granular activated carbon system was installed, there is also a specific limit of 2.4 mg/l of fluoride. This directive is consistant with similar actions presently underway in many states including Arizona, California, Texas relating to fluoride in potable ground water supplies. The purpose of this study was to determine the techno-economic feasibility of the activated alumina process to remove excess fluoride from the carbon treated water. The study included data on pH and fluoride levels of the raw and treated water through two (2) exhaustion cycles of the alumina and two chemical regeneration cycles.

Preliminary chemical usage, operating and capital costs are presented along with the test analytical results.

II. Test Description

A. General Procedures.

The test apparatus schematically shown in Appendix F was installed on September 11, 1978 adjacent to the activated carbon system in the north boundary treatment building and was operated through September 23, 1978.

The test apparatus included a ten-inch diameter by five foot high PVC column containing one cubic foot of activated alumina (Alcoa F-1, 28 x 48 mesh).

During each run the pH of the carbon treated water was adjusted downward by the addition of H_2SO_4 and the water then passed downflow through the alumina at a flow rate between 1.5 and 1.6 gpm. Samples of the pH adjusted raw water and treated water were periodically examined for fluoride and pH levels.

Comparative analyses between on-site fluoride tests and RMA analytical laboratories indicated a very close correlation throughout the study (see Appendix G).

Samples of the regeneration effluent were collected in 50 and 100 gallon composites and the concentration of the fluoride determined.

B. Discussion.

Removal of fluoride from the carbon treated water by the activated alumina process proceeded as expected during the first run achieving levels of 0.25 mg/l for part of the run. In all 13,320 gallons were treated with an

average fluoride level of 1.04 mg/l (Appendix A). This represents an alumina capacity of 2,781 grains per cubic foot.

Regeneration of the alumina following the first run proceeded normally but the pH of the effluent solution did not achieve expected levels of 12+. Analysis of the composite sample regeneration fluids indicated incomplete removal of fluoride from the bed. Therefore, a second regeneration was performed. Data (Appendix C) indicates that 2,400 grains of fluoride were recovered from both regenerations. This represents 85% of the total fluoride removed during the first run. In the second run as in the first, fluoride levels reached the 0.25 mg/l level for a portion of the run and 11,325 gallons were treated with an average fluoride concentration of 1.00 mg/l. This represents a capacity of 2,440 grains of fluoride per cubic foot of alumina.

The second regeneration of the alumina proceeded normally. Data on the composite sample of regenerate solution indicated a total recovery of 1,880 grains of fluoride. Again as in the first regeneration, this represents incomplete (79%) recovery of the fluoride from the bed.

An additional regeneration test was performed on the alumina bed which had undergone the aforementioned two exhaustion and two regeneration cycles. One tenth (1/10) of a cubic foot of alumina was placed in a two-inch column

fluoride was removed which would equate to 530 grains in the one cubic foot test bed of alumina. Since 1,880 grains had previously been extracted, the total recovery extrapolates to 2,410. This compares reasonably well to the total fluoride removed during the second exhaustion cycle of 2,440 grains per cubic foot.

While outside the scope of this study, tests for other chemical constituents such as boron and total organic carbon (TOC) indicate some variability in the quality of the water being treated. The drop in fluoride removal capacity of the alumina (2,781 to 2,440 grains per cubic foot) between Run I and II suggest the presence of chemical constituents which compete with fluoride for alumina sites.

III. Preliminary Process Design

The following parameters were used to outline a proposed full-scale treatment facility:

1.	Location:	Northeast corner of the carbon treatment building at north boundary. Treatment units inside - chemical storage outside.
2.	Pumping:	Provided by carbon system.
3.	Backwashing Water:	Taken from effluent of on-stream carbon. treatment units.

4.	Utilities:	Electrical - within building.
		Air - within building.
		Water - carbon treated effluent.
5.	Operator:	Available from present staff.
6.	Chemical Delivery:	From bulk trucks.
7.	Flow Rate:	80 - 200 gpm.
8.	Wastewater Handling:	Evaporation pond.
9.	Instrumentation:	Flow regulator and totalizer, pH controller and indicator.

The treatment units would consist of four (4) adsorbers containing 140 cubic feet of activated alumina with appropriate underdrain piping and head room to allow periodic backwashing. A day tank will feed acid in proportion to the flow and in response to pH controllers. The acidified water will be processed downflow in three of the four tanks. The fourth unit will be in reserve each cycle.

Acid and caustic storage tanks located outside and adjacent to the alumina process equipment will supply chemicals to the day tanks. Caustic regeneration of the alumina will occur for the first of the treatment vessels when the blended effluent approaches the treatment objective of 1 mg/l. Each alumina bed will be placed in service on a staggered startup basis to effect sequential exhaustion of each of the four treatment beds. This allows blending of effluents for greater economy.

Regenerate fluids including rinse waters will be diverted to a lined evaporation pond adjacent to the treatment building.

The existing carbon plant operations personnel will be required to monitor performance, fill the day tanks, take samples, and to perform regeneration procedures.

IV. Capital and Operating Cost Projections

A. Capital Costs.

Process Equipment		$60,000.00
Treatment vessels	$15,000.00	
Process piping and instrumentation	15,000.00	
Activated alumina	8,000.00	
Chemical storage vessels	15,000.00	
Chemical pumps, piping and accessories	7,000.00	
Process Equipment Installation		32,000.00
Lined Evaporation Pond		50,000.00
	Subtotal	$142,000.00
Contingency and Contractors Profit		20,000.00
Engineering		25,000.00
Services	20,000.00	
Expenses	5,000.00	
	TOTAL	$187,000.00

*Based upon September 1978 prices

B. Operating Costs.

The chemical costs developed during the study are summarized in Appendix E. These data are based upon an average capacity of 2,600 grains per cubic foot of alumina for removal of 5.0 to 4.0 mg/l of fluoride to a 1 mg/l average level. The projected acid consumption can be extrapolated from the test results (Appendix E) with reasonable certainty. On the other hand, caustic consumption during the test was not firmly established. Higher than normal amounts of regenerate was used in the first cycle regeneration. Additionally, the second cycle exhausted alumina did not release all of the fluoride removed in the second cycle. Until additional testing develops more precise data, it is necessary to project higher than normal caustic costs. Therefore, the projected costs which follow assume the caustic requirements to be that used during the test. Additionally, the working capacity is projected at 2,000 grains per cubic foot which is only 75% obtained during the study.

Using these parameters the operating costs can be projected as follows:

	$ per 1,000 Gallons
1. Chemicals	
66 Be H_2SO_4 @ $60/Ton	$0.056
50% NaOH $205/Ton	0.136
2. Alumina Replacement	
3% per year @ 40¢ pound	0.010

3.	Operator (existing)	--
4.	Electricity (existing)	--
5.	Miscellaneous Supplies/Service	0.02
		$.212

The high caustic regeneration projected costs results from a higher price for caustic in truck deliveries vs. rail (205/Ton vs. $179/Ton) and inefficient caustic regeneration during the test. Further study should develop more effective regeneration procedure and thus reduce operating costs.

V. Conclusions and Recommendations

Using the activated alumina process, this study demonstrated that excess fluoride can be removed from the carbon treated water at the reinjection site of the northern boundary of the Rocky Mountain Arsenal. This study consisting of two complete treatment cycles including chemical regeneration demonstrated the removal of fluoride from levels of 4-5 mg/l to an average 1 mg/l or less. Additionally, a capacity of more than 2,000 grains of fluoride per cubic foot of alumina was achieved. This fluoride removal performance is better than the specific limitations cited by the EPA and the Colorado Department of Health of 2.4 mg/l.

A full-scale treatment plant rated for 80-200 gallons per minute is projected to cost $187,000.00 for engineering design, installation and start-up. Operating costs are pro-

jected to be 21 cents per 1,000 gallons utilizing the existing personnel and available pumping. Improved operating costs are likely to be developed if additional cyclic tests are performed to optimize caustic regeneration.

A lined evaporation pond was included in the capital cost projections since this method of wastewater handling has been used successfully in Arizona projects. There are other methods of disposal which can be considered if evaporation ponds are inappropriate at this site.

It is recommended that the Rocky Mountain Arsenal proceed with the design and installation of a full-scale fluoride system in order to comply with Colorado Department of Health directives.

Concurrent to the engineering design effort, a laboratory study is recommended to analyze the retained samples from this study of raw and treated water along with regenerate fluid to determine if any other chemical constituents (in addition to fluoride) are being retained on the alumina and/or released during regeneration.

Based on these analyses additional alumina exhaustion and regeneration cycles should then be performed to optimize the caustic regeneration procedure for maximum long term economy.

LIST OF APPENDICES

APPENDIX A

TEST RUN NO. 1 DATA TABULATION

Time (hrs:min)	Δ Gals Treated	Total Gals Treated	Adj RW pH	TW pH	RW F mg/l	TW F mg/l	Δ Ave F mg/l	Δ Grains Removed	Total Grains Removed	TW Ave F mg/l
0:00	0	0	5.0	10+	4.1					
0:30	50	50	5.0	8.2		0.95	0.95	9	9	0.95
1:00	50	100	5.0	7.8	4.1	0.70	0.87	10	19	0.91
1:30	40	140	5.0	7.6		0.68	0.69	8	27	0.84
2:15	60	200	5.5	7.5		0.66	0.67	12	39	0.79
2:45	50	250	5.5	7.5		0.61	0.63	10	49	0.76
7:15	400	650	5.5	6.5		0.25	0.43	86	135	0.55
14:15	610	1260	5.5	5.9		0.25	0.25	138	273	0.41
18:15	360	1620	5.5	5.8		0.25	0.25	82	355	0.37
19:15	90	1710	5.5	5.8		0.25	0.25	20	375	0.37
22:15	270	1980	5.5	5.7		0.25	0.25	61	436	0.35
24:45	180	2160	5.5	5.7		0.30	0.27	41	477	0.34
28:45	390	2550	5.5	5.6	4.8	0.30	0.30	103	580	0.34
32:45	390	2940	5.5	5.6		0.25	0.28	94	674	0.33
38:45	610	3550	5.5	5.5		0.25	0.25	163	837	0.32
42:15	350	3900	5.5	5.5	4.6	0.25	0.25	89	926	0.31
44:15	190	4090	5.5	5.5		0.30	0.28	48	974	0.31
47:45	360	4450	5.5	5.5		0.30	0.30	91	1065	0.31
51:15	350	4800	5.5	5.5		0.30	0.30	89	1154	0.31
56:15	510	5310	5.5	5.5		0.35	0.32	128	1282	0.31
62:45	650	5960	5.5	5.5	5.0	0.50	0.43	175	1457	0.32
67:15	440	6400	5.5	5.5	4.9	0.70	0.60	111	1568	0.34
69:15	200	6600	5.5	5.5		0.72	0.71	49	1617	0.35
72:15	300	6900	5.5	5.5	4.8	0.82	0.77	71	1688	0.37
73:15	100	7000	5.5	5.5		0.85	0.83	23	1711	0.38
76:15	300	7300	5.5	5.5		0.83	0.86	69	1780	0.40
78:15	200	7500	5.5	5.5	5.0	0.93	0.91	48	1828	0.41
81:15	290	7790	5.5	5.5		0.98	0.95	69	1897	0.43

APPENDIX A

TEST RUN NO. 1 DATA TABULATION

Time (hrs:min)	Δ Gals Treated	Total Gals Treated	Adj RW pH	TW pH	RW F mg/l	TW F mg/l	Δ Ave F mg/l	Δ Grains Removed	Total Grains Removed	TW Ave F mg/l
87:00	600	8390	5.5	5.5	4.6	1.15	1.05	125	2022	0.47
91:45	458	8848	5.5	5.5	4.6	1.35	1.25	90	2112	0.51
95:45	422	9270	5.5	5.5	4.75	1.55	1.45	82	2194	0.56
97:15	140	9410	5.5	5.5		1.80	1.67	25	2219	0.57
98:45	560	9970	5.5	5.5		1.90	1.85	96	2315	0.64
102:45	800	10770	5.5	5.5	4.90	1.95	1.92	140	2455	0.74
114:45	200	10970	5.5	5.5		2.10	1.04	45	2500	0.75
119:45	510	11480	5.5	5.5		2.20	2.15	83	2583	0.81
123:45	390	11870	5.5	5.5	4.70	2.50	2.35	54	2637	0.86
129:15	900	12770	5.5	5.5		2.80	2.65	93	2730	0.98
135:15	460	13230	5.5	5.5		2.80	2.80	51	2781	1.04

APPENDIX B

TEST RUN NO. 2 DATA TABULATION

Time (hrs:min)	Δ Gals Treated	Total Gals Treated	Adj RW pH	TW pH	RW F mg/l	TW F mg/l	Δ Ave F mg/l	Δ Grains Removed	Total Grains Removed	TW Ave F mg/l
0:00				11.8	4.7	5.0				
0:15	20	20	3.0	11.4		2.2	3.6	1	1	3.60
0:30	45	65		11.2		1.5	1.8	8	9	2.3
1:00	47	112	3.0	10.8		0.58	1.0	10	19	1.6
5:15	413	525	4.5	6.4		0.25	0.42	104	123	0.67
6:45	133	658	5.5	5.6		0.25	0.25	35	158	0.59
11:15	559	1217	5.5	5.6		0.25	0.25	146	304	0.43
12:15	101	1318	5.5	5.6		0.25	0.25	26	330	0.42
12:45	50	1368	5.5	5.6	4.7	0.25	0.25	13	343	0.41
16:45	405	1773	5.5	5.5		0.25	0.25	106	449	0.37
21:30	487	2260	5.5	5.5		0.25	0.25	127	576	0.35
29:00	770	3030	5.5	5.5		0.25	0.25	202	778	0.32
33:15	525	3555	5.5	5.5	4.7	0.25	0.25	137	915	0.31
37:15	405	3960	5.5	5.5		0.25	0.25	106	1021	0.30
41:15	395	4355	5.5	5.5		0.30	0.27	103	1124	0.30
45:15	312	4667	5.5	5.5		0.35	0.33	80	1204	0.30
54:15	923	5590	5.5	5.5	4.7	0.60	0.47	230	1434	0.33
59:15	400	5990	5.5	5.5		0.75	0.67	93	1527	0.35
64:15	500	6490	5.5	5.5		0.90	0.82	114	1641	0.39
68:15	500	6990	5.5	5.5		1.00	0.95	110	1751	0.43
72:15	395	7385	5.5	5.5		1.40	1.20	81	1832	0.47
77:45	405	7790	5.5	5.5		1.60	1.50	100	1932	0.52
79:4[illegible]	260	8050	5.5	5.5		1.70	1.65	47	1978	0.56
83:15	350	8400	5.5	5.5		1.80	1.75	61	2040	0.61
87:15	400	8800	5.5	5.5		1.90	1.85	67	2107	0.67

APPENDIX B

TEST RUN NO. 2 DATA TABULATION

Time (hrs:min)	Δ Gals Treated	Total Gals Treated	Adj RW pH	TW pH	RW F mg/1	TW F mg/1	Δ Ave F mg/1	Δ Grains Removed	Total Grains Removed	TW Ave F mg/1
90:15	290	9090	5.5	5.5		2.0	1.95	47	2154	0.70
94:15	300	9390	5.5	5.5		2.2	2.10	46	2200	0.75
102:45	710	10100	5.5	5.5		2.3	2.25	102	2224	0.86
104:15	170	10270	5.5	5.5		2.3	2.3	24	2248	0.88
107:15	260	10530	5.5	5.5		2.3	2.3	37	2285	0.91
111:15	375	10905	5.5	5.5		2.3	2.3	53	2338	0.96
115:00	375	11325	5.5	5.5		2.4	2.35	51	2440	1.00

APPENDIX C

REGENERATION OF ACTIVATED ALUMINA

FOLLOWING TEST RUN NO. 1

Time (hrs:min)	Total Gals Caustic	Total Gals Rinse	gpm/ft²	TW pH	Δ Gr F	
0:00			4.8			Start rinse
0:20		52				Stop rinse - drain tank
1:00			1.1			Start regeneration solution upflow
1:28	17[a)]					Stop regeneration solution
1:42			2.8			Start rinse - collect in 55 gallon barrel
1:45				11.4		Too low!
1:55				11.2		
2:03				10.6		
2:15		55		9.6	734	First barrel full F = 240 mg/l
						Start second barrel
2:25				9.2		
2:35			4.6	9.0		Increased flow
2:45		55		8.6	291	Second barrel full F = 90 ppm - stop rinse
3:05			1.1			Start regeneration solution downflow
3:33	17[b)]			11.6		Stop regeneration solution
4:31			2.8			Start downflow rinse
7:15		200		9.2		Stop rinse
					676	Composite 100 gallons F = 115 mg/l
					64	Composite 100 gallons F = 11 mg/l
7:20			1.1			Insufficient F recovery - start regeneration
7:48	17[c)]			11.5		
7:50			0.9			Start additional downflow regeneration solut
8:18	10[d)]			12+		Start rinse
10:03		98			808	Composite 125 gallons F = 110 mg/l

Total F Recovery = 2573 gr

a) 900 ml of 50% NaOH in 17 gallons of water
b) 1100 ml of 50% NaOH in 17 gallons of water
c) 1100 ml of 50% NaOH in 17 gallons of water
d) 1100 ml of 50% NaOH in 10 gallons of water

APPENDIX D

REGENERATION OF ACTIVATED ALUMINA

FOLLOWING TEST RUN NO. 2

Time (hrs:min)	Total Gals Caustic	Total Gals Rinse	$\frac{gpm}{ft^2}$	TW pH	Δ Gr F	
0:00						Drain tank
0:20			1.1			Start upflow regeneration solution
0:50	20[a]		3.7			Stop regeneration solution - start rinse and collect in 55 gallon barrel
0:57				7.5		
1:00				12+		
1:13				12		
1:25		55		11.6	1219	Barrel full F - 375 mg/l
1:40				11.5		
1:53					244	Second barrel full F = 112 mg/l - stop upflow rinse
2:15			1.1			Start downflow regeneration solution
2:30	20[b]					Stop regeneration solution - start downflow rinse
3:30				11.4		Increase flow
3:50				10.8		
4:05		200		10.6		Stop rinse
					382	Composite 100 gallons rinse F = 65 mg/l
					35	Composite 100 gallons rinse F = 6 mg/l

Total F Recovery = 1880 gr

a) 1550 ml of 50% NaOH in 20 gallons of water
b) 1550 ml of 50% NaOH in 20 gallons of water

APPENDIX E

CHEMICAL CONSUMPTION DATA - FEASIBILITY STUDY

Acid

Run No. 1	4,700 ml 66° Be H_2SO_4	for 13,230 gallons of treated water
Run No. 2	4,000 ml	for 11,325 gallons of treated water
	8,700	24,555

2,298 gallons per 24,555 gallons of treated water
0.092 gallons per/1,000 gallons of treated water
1.38 gallons per/1,000 gallons of treated water

@ \$60/Ton = 0.041 cents per/1,000 gallons of treated water

Caustic

Regeneration No. 1	4,200 ml 50% NaOH
No. 2	3,100 ml 50% NaOH
	7,300 per 24,555 gallons of treated water

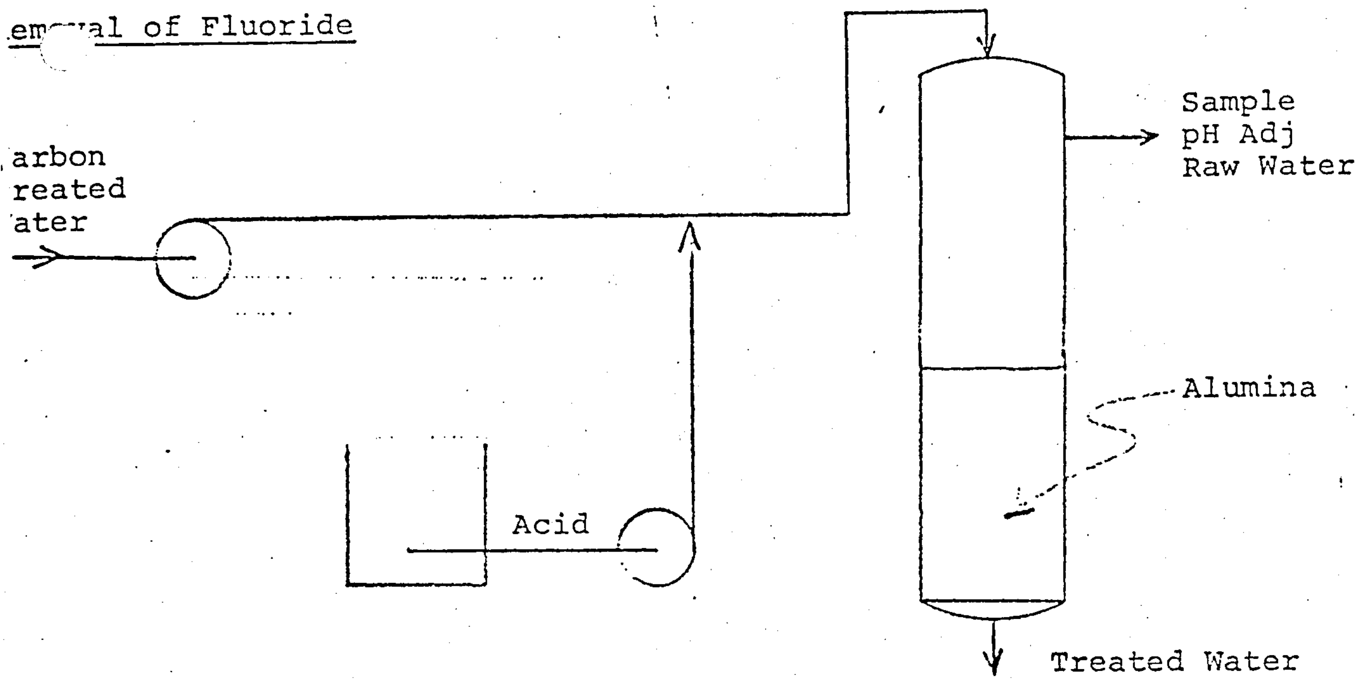
1929. gallons per 24,500 gallons of treated water
0.077 gallons per/1,000 gallons of treated water

0.98 pounds per/1,000 gallons of treated water

@ \$205/Ton = 0.1[illegible] cents [illegible] 000 ggallons of treated water

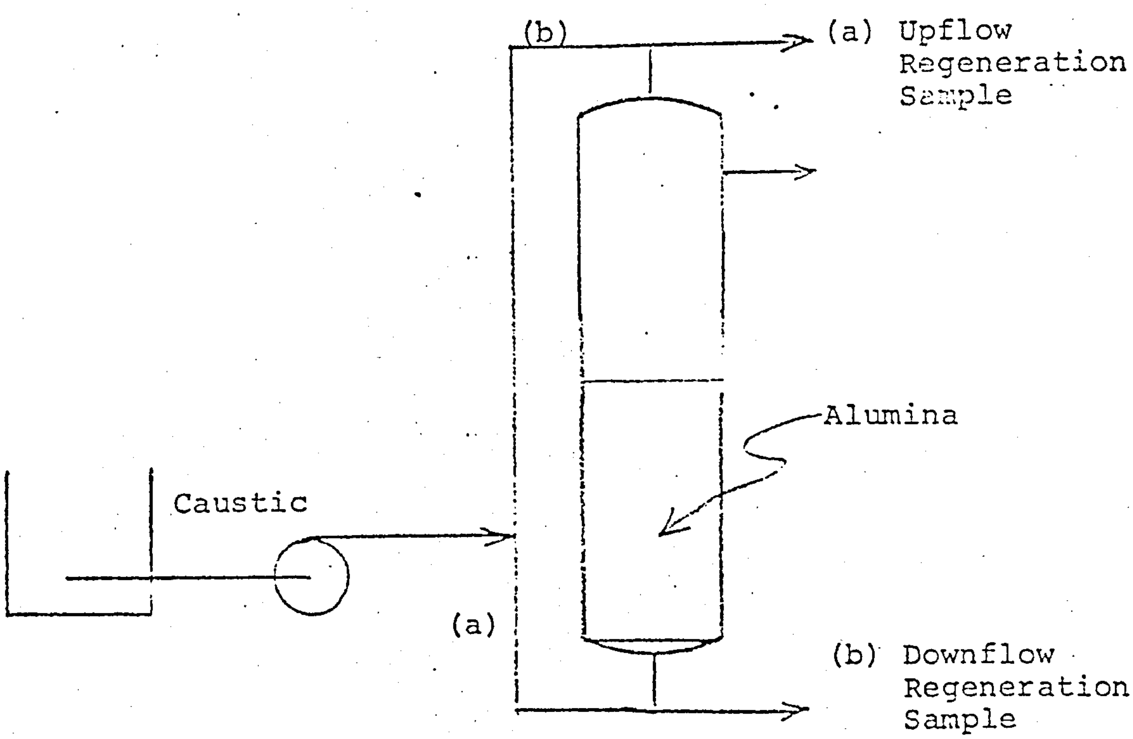
TEST APPARATUS SCHEMATIC

emoval of Fluoride



egeneration Cycle

(a) Upflow
(b) Downflow



APPENDIX G

FLOURIDE ANALYSES COMPARISONS

Sample No.	Gallons Treated	On Site Analysis* mg/l	RMA Specific ion mg/l	RMA Technicon mg/l
Run No. 1				
1	140	0.68	0.15	less than 0.20
2	650	0.25	less than 0.10	less than 0.20
3	1,260	0.25	less than 0.10	less than 0.20
4	3,550	0.25	less than 0.10	less than 0.20
5	5,310	0.35	0.12	less than 0.20
6	5,960	0.50	0.46	0.50
7	6,900	0.82	0.56	0.59
8	8,390	1.15	1.10	1.17
9	9,270	1.55	1.40	1.49
10	9,970	1.90	1.64	1.71
11	10,970	2.10	2.00	2.04
[illegible]	11,870	2.50	2.16	2.24
13	13,230	2.80	2.69	2.87
Run No. 2				
1	320		1.58	1.64
2	830	0.25	0.35	0.34
3	2,063	0.25	less than 0.10	less than 0.20
4	3,030	0.25	less than 0.10	less than 0.20
5	4,667	0.35	0.18	0.20
6	5,590	0.60	0.60	0.62
7	6,490	0.90	1.21	1.14
8	8,800	1.90	2.10	1.91
9	10,100	2.30	2.20	2.16

* Hach DR 2 Spectrophotometer

COLORADO DEPARTMENT OF HEALTH
4210 EAST 11TH AVENUE • DENVER, COLORADO 80220 • PHONE 388-6111
Anthony Robbins, M.D., M.P.A. Executive Director

May 27, 1977

Colonel Byrne
Commanding Officer
Rocky Mountain Arsenal
Denver, Colorado 80240

Colonel Byrne:

Several times in the past, Arsenal personnel have requested guidance on the quality of the reinjection water at the north boundary of the Rocky Mountain Arsenal.

After consideration of water use in the area north of the Rocky Mountain Arsenal, it was concluded that the quality of the reinjected water should be subject to drinking water standards. State drinking water limitations are contained in part 5 of "Standards for the Quality of Water Supplied to the Public", a copy of which is attached. The fluoride level contained in this part is incorrect and should be 2.4 mg/l as directed by Section 141.11(c) of the December 24, 1975 federal register entitled "Water Programs". In addition, Section 141.12 addresses levels for organic chemicals which should be met.

The Colorado Department of Health has reviewed the findings of the National Academy of Science relative to temporary guidelines for DIMP and DCPD in drinking waters. Based on toxicity, this Department is in agreement with the 0.3 ppm DIMP and 1.28 ppm DCPD limits. However, due to odors associated with DCPD, the reinjected water will be subject to the threshold odor number of 3, directed by part 4 of the State regulations.

If there are any questions, please contact this Department.

Very truly yours,

Robert D. Siek
Assistant Director, Department of Health
Environmental Health

RDS:RJS/emf

<u>APPENDIX I-A</u>

LABORATORY EVALUATION 30 GALLON BARREL

(.01 ft^3 alumina 28 x 48 mesh)

	Time	Adjusted RW pH	RW F mg/l	TW F mg/l	TW pH	
8/9/78	11:00 a.m.	7.8	3.9			Start downflow 40 Ml per mi
	11:30 a.m.			1.1	8.9	
	1:30 p.m.	4.0		0.6	8.5	Adjust acid feed
	2:30 p.m.	5.5		0.4	8.2	Adjust acid feed
	4:30 p.m.			0.35	8.0	
	7:00 p.m.			0.35	7.7	
	9:00 p.m.			0.30	7.6	Flow off
8/10/78	9:00 a.m.		3.9			Flow on 40 Ml per minute
	9:15 a.m.	4.0		0.45	7.8	Adjust acid feed
	11:00 a.m.			0.4	7.2	
	1:00 p.m.			0.3	6.8	
	3:00 p.m.			0.25	6.8	Sample depleted

CONCLUSION: The process functions normally on this water and on-site cyclic test are recommended to verify alumina capacity for fluoride removal.

APPENDIX I-B

ANALYSIS OF 30 GALLON BARREL

ROCKY MOUNTAIN ARSENAL CARBON TREATMENT EFFLUENT

Dissolved Solids @ 180°C mg/l	1500
Nitrate Nitrogen as N	less than 0.05
Total Phosphate as P	2.8
Boron	0.5
Fluoride	3.5
Hardness as $CaCO_3$	480
Arsenic	less than 0.01
Barium	less than 0.1
Cobalt	0.05
Manganese	0.80
Selenium	0.012
Zinc	0.30
Total Organic Carbon	15

COMPARISON OF CHEMICAL ANALYTIC INSTRUMENTS USED IN PILOT STUDIES OF FLUORIDE REMOVAL IN CALGON PLANT ADSORBER EFFLUENT

This section of the "Fluoride Removal Report" compares the three analytical techniques used to determine the fluoride levels found in alumina adsorption column work. Specifically, the values for fluoride levels are found with the Hach DR2 Spectrophotometer in the Ruebel and Hager, Inc., alumina adsorption column studies are compared against the values for the fluoride levels as found at RMA using the specific ion probe method and the Technicon Colorimetric method. The purpose of this comparison is primarily to check the veracity of the Ruebel and Hager, Inc. studies. A secondary purpose is to set numbers on the differences in fluoride readings between the different methods.

The tabulated data on the two runs made by Ruebel and Hager, Inc. is given in Appendix G (Pg 45 herein) for the three methods used. This is followed by Figures 10 and 11 which are a plot of fluoride levels versus total gallons passed thru the alumina column used by Ruebel and Hager, Inc.

TABLE VI

	Average Differential Values (mg/l)					
un No.	Specific Ion	vs Hach DR2	Technicon	vs Hach DR2	Specific Ion	vs Technicon
. Activated	0.1938*	1.28%	0.1146	0.76%	0.079	0.58%
. Regenerated	0.005	0.033%	0.00375	0.025%	0.0011	0.008%

* - Absolute Value - only magnitude considered.

As can be seen by Table VI the readings taken by the Hach DR2 Spectrophotometer are in close agreement with those taken by the Specific Ion Probe

method and the Technicon colorimetric method. This close agreement (1.25% maximum) verifies the work of Ruebel and Hager, Inc. The average difference numbers obtained allow future readings to be directly correlated to each other.

Another comparison is made of the plots (fluoride levels versus gallons passed thru the alumina column) using the readings obtained by the three different methods. A glance at each of the two graphs, Figures 10 and 11, show the graphs in each instance have nearly the same characteristic shape on each run with the slopes at any point staying close. The chance of this corrspondence occurring randomly is very minute. The probability is very high that the Hach DR2 curve is the correct image of the change in the fluoride levels thru the alumina column.

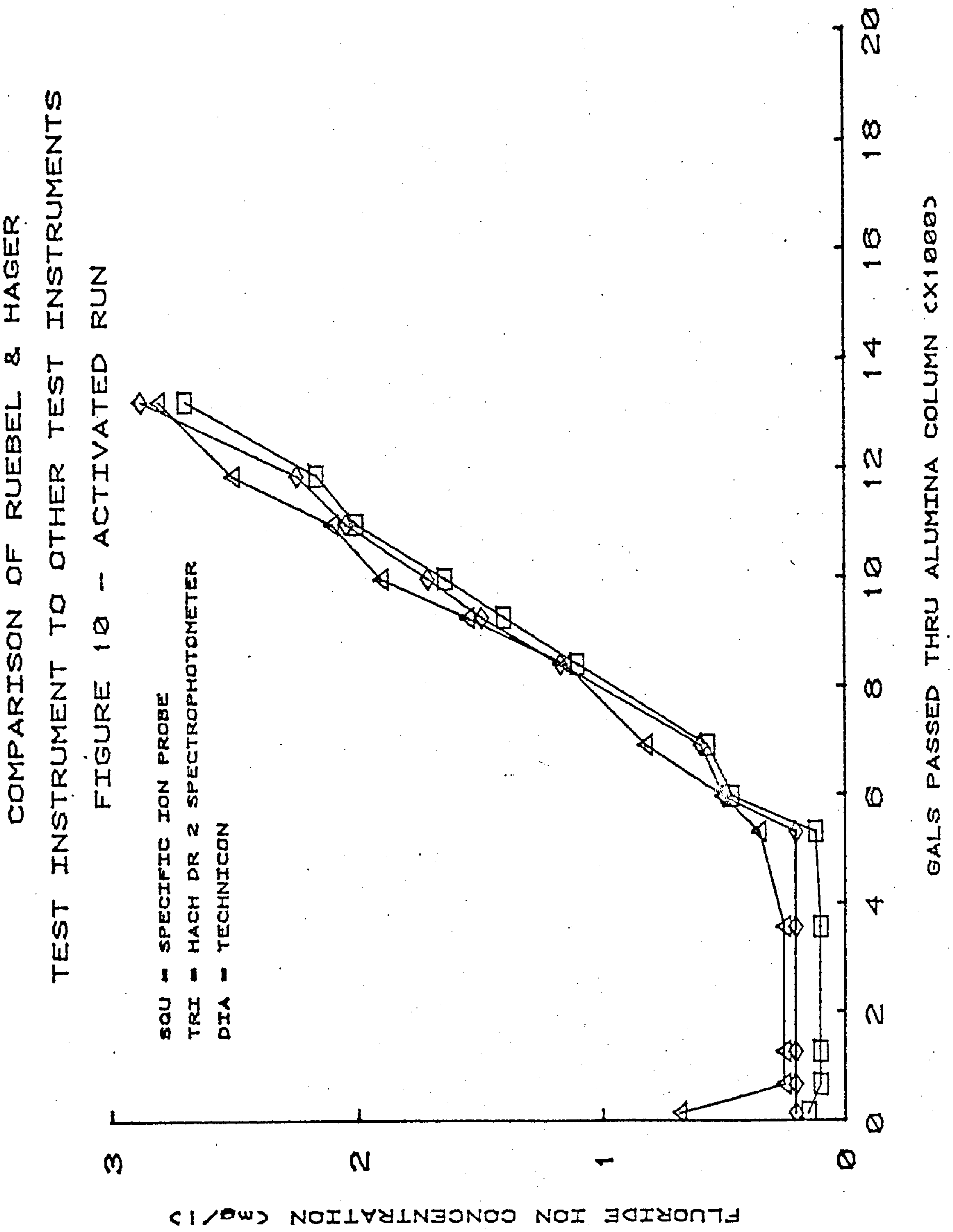

COMPARISON OF RUEBEL & HAGER
TEST INSTRUMENT TO OTHER TEST INSTRUMENTS
FIGURE 10 - ACTIVATED RUN
SQU = SPECIFIC ION PROBE
TRI = HACH DR 2 SPECTROPHOTOMETER
DIA = TECHNICON
FLUORIDE ION CONCENTRATION (mg/l)
0
1
2
3
0
2
4
6
8
10
12
14
16
18
20
GALS PASSED THRU ALUMINA COLUMN (X1000)

FIGURE 10

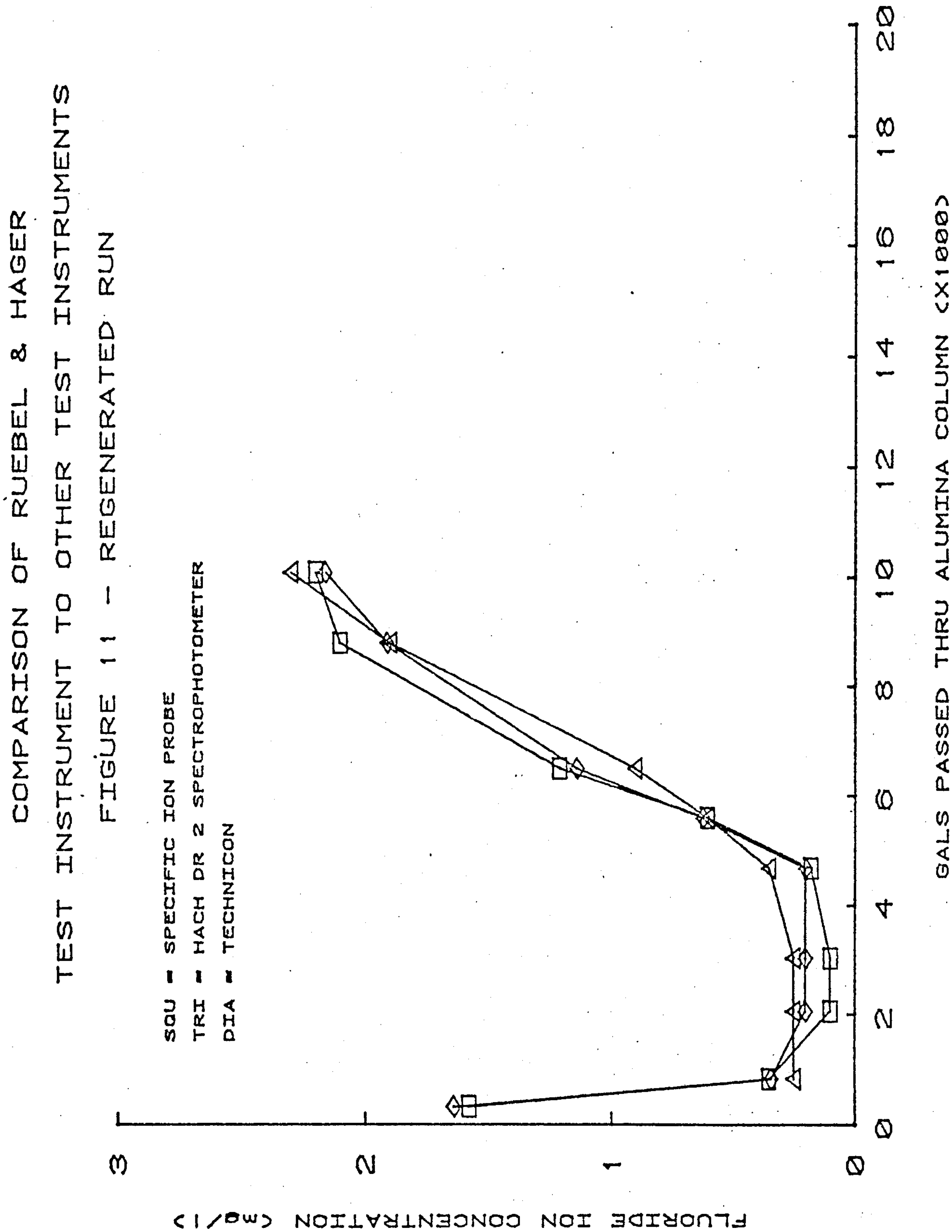

COMPARISON OF RUEBEL & HAGER
TEST INSTRUMENT TO OTHER TEST INSTRUMENTS
FIGURE 11 - REGENERATED RUN
SQU = SPECIFIC ION PROBE
TRI = HACH DR 2 SPECTROPHOTOMETER
DIA = TECHNICON
FLUORIDE ION CONCENTRATION (mg/l)
0
1
2
3
GALS PASSED THRU ALUMINA COLUMN (X1000)
0
2
4
6
8
10
12
14
16
18
20

FIGURE 11

ISOTHERM RUNS ON DIFFERENT TYPES OF ALUMINAS TO DETERMINE THE HIGHEST LOADING CAPACITY

In order to accelerate the fluoride removal program a series of isotherm tests were developed. These tests would show which of the several available aluminas had the greatest loading capacity and thus the greatest likelihood of being the highest performer in fluoride removal.

The outline of this phase of the fluoride removal program was (1) make a search of industrial sources selecting the alumina(s) recommended by the technical representatives of each company (2) set up isotherm runs with selected alumina, and (3) analyze the results of the isotherm run to compare the ultimate loading capacity of each alumina so as to select the alumina having the highest loading capacity. Contact was made with the three companies found to be primary sources of alumina, ie, MCB, Kaiser Aluminum and ALCOA, and samples of recommended aluminas were sent to PD&E Division at RMA for isotherm tests.

The isotherm tests were set up and followed the following methodology:

(1) 500 milliters of Calgon plant adsorber effluent water was measured into a 1 liter jar,

(2) Various amounts of alumina* were weighed and placed into each jar with one jar not receiving any alumina**,

(3) Timers and stirrers were simultaneously started,

(4) After a set period, stirrers were stopped and elapsed time recorded,

(5) Water in 1 liter jars was filtered,

* Efficient stirring could not be obtained with natural state alumina so alumina needed to be crushed and sieve graded.

** This was a blank used as a control.

(6) Fluoride levels were tested and recorded, and

(7) Fluoride levels, volume of water and weight of alumina used in the sample were used to obtain a Freundlich equation plot. The Freundlich equation is $x/m = K\,C^{1/n}$, where: x = amount of fluoride adsorbed, m = weight of alumina, K and N are constants, and C = unadsorbed fluoride concentration in solution. When plotted on log-log paper, the Freundlich equation reduces to a straight line equation of the form $y = b + mx$ with $y = \log(x/m)$, $b = \log k$, $x = c$ and m (the slope) = $1/n$. A x/m ultimate value can be found at the point where C = untreated fluoride concentration and thus the loading capacity is found.

The tabulized date from the isotherm test is given in Table VII below and the isotherm plot follows in Figure 12:

TABLE VII

Type Alumina	Grams Used	Remaining F Concentration (mg/l)
MCB Crushed Spheres* (8 x 14 Mesh)	1 3 10 30	1.75 .74 .42 1.20
Kaiser A-300 Ungranulated	1 3 10 30	.85 .32 .19 .21
Kaiser A-301 Spheres*	1 3 10 30	1.18 .64 .29 .31
ALCOA F-1 (28-48 Mesh)	1 3 10 30	1.35 .76 .42 .79
MCB Crushed Spheres (8X14 Mesh) Crushed Finer	1 10 30	2.00 .49 1.14
Kaiser A-301 Spheres (crushed)	1 3 7 12	1.16 .58 .30 .29
Control Sample	0.0	4.15

* It was not possible to maintain constant stirring with these aluminas in their original state so the method of crushing to a graded powder was used.

FIGURE 12

ALUMINA ISOTHERMS

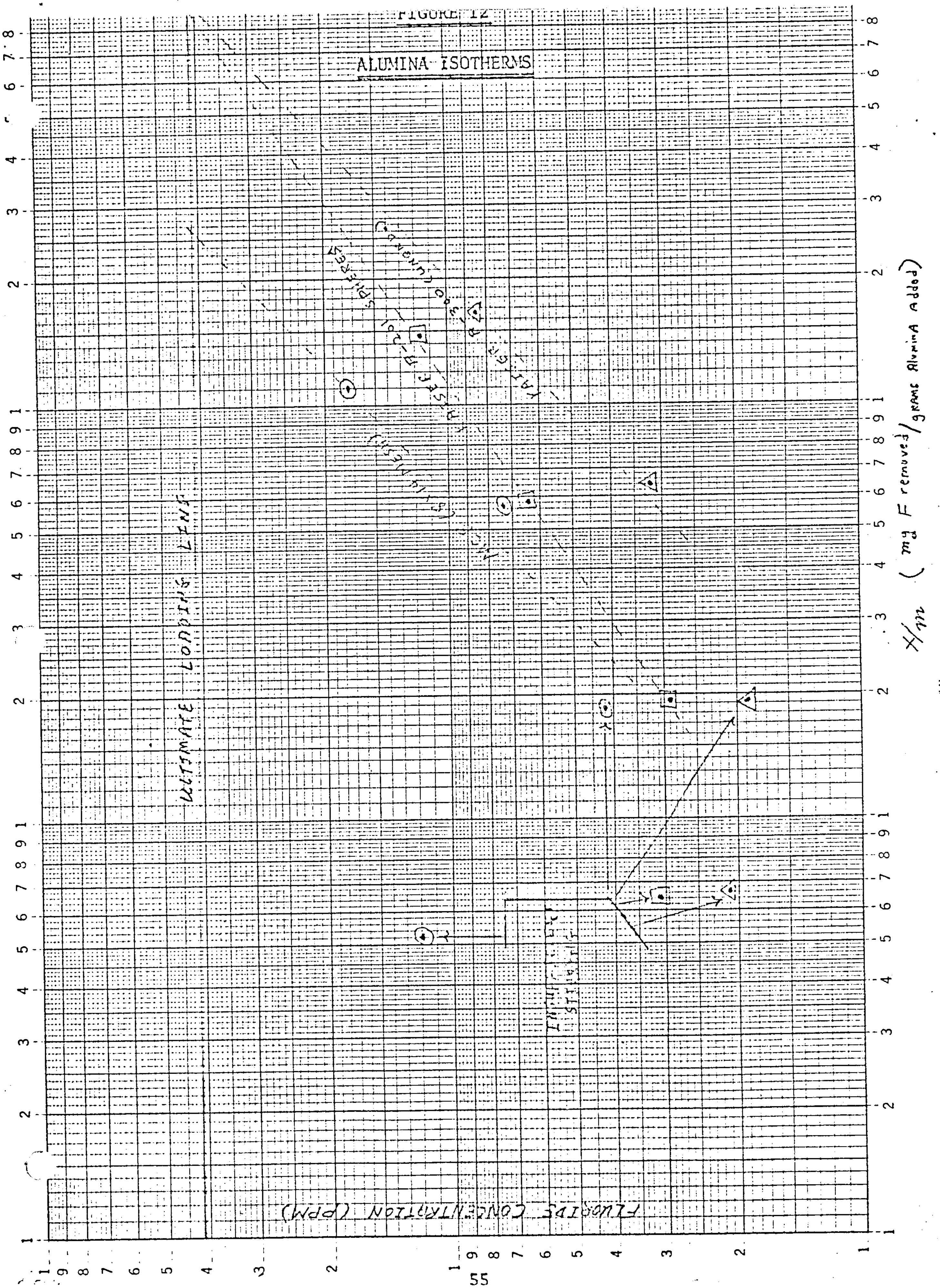
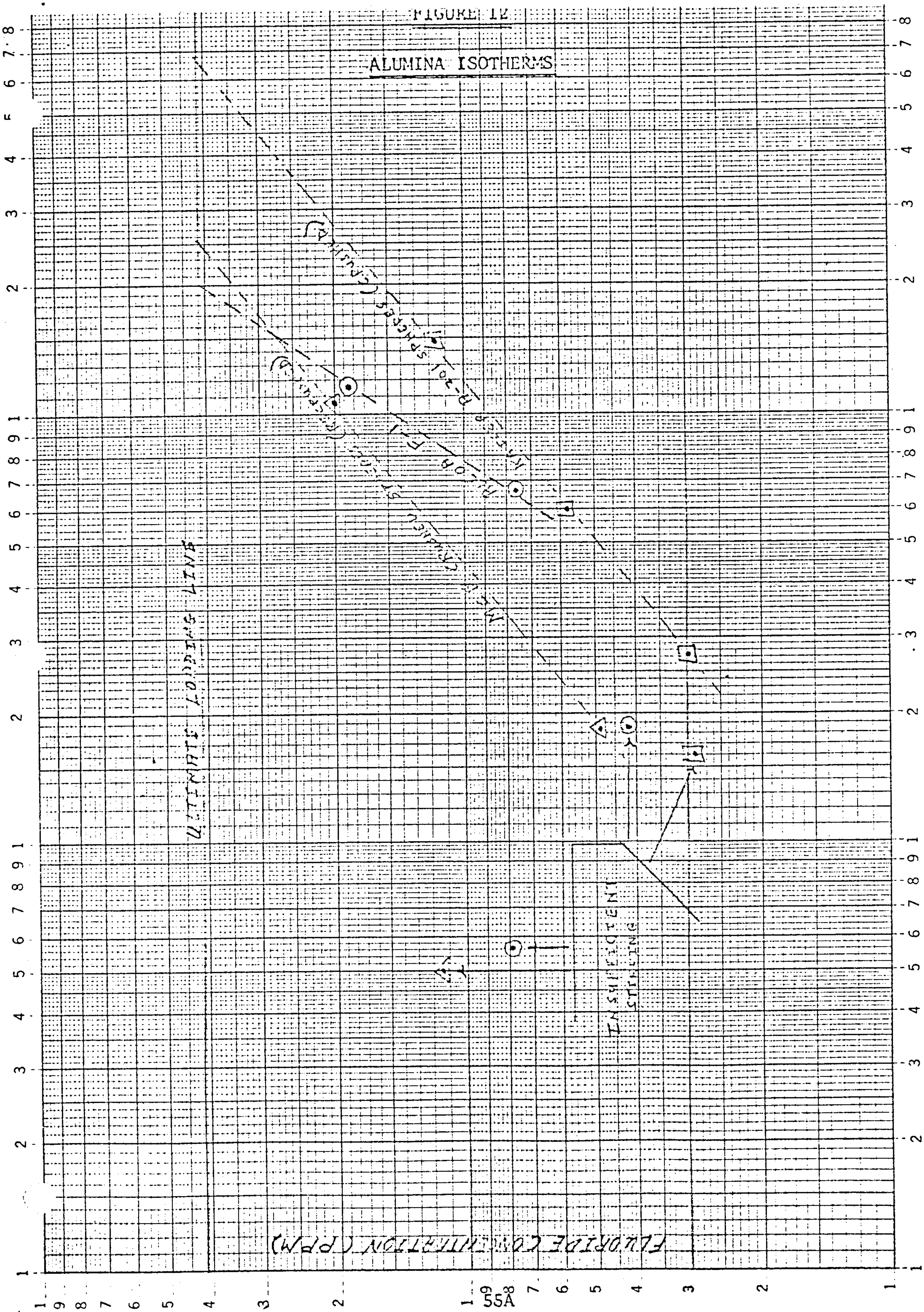


FIGURE 12

ALUMINA ISOTHERMS



Once the Freundlich equation plot had been made it was possible to determine the $(^x/m)$ ultimate value for each alumina and the $^1/n$ and K constant values. The results from the Freundlich equation plot (Figure 12) are given in Table VIII below:

TABLE VIII

VALUES OF ISOTHERM PARAMETERS FOR DIFFERENT ALUMINAS

Type Alumina	$^1/n$ Value	K Value	$(^x/m$ Ultimate
MCB Crushed Spheres (8 x 14 Mesh)	.45	1.393	2.60 (mg/g)
Kaiser A-300 Ungrd.	1.8	.577	7.00 (mg/g)
Kaiser A-301 Spheres	1.7	1.137	12.0 (mg/g)
ALCOA F-1 (28 x 48 Mesh)	.65	.922	2.27 (mg/g)
MCB Crush Spheres (Crushed Fine)	.55	1.096	2.35 (mg/g)
Kaiser A-301 Spheres Crushed	1.25	1.343	7.60 (mg/g)

In evaluating the parameters given in Table VIII above the following facts are taken into consideration:

(1) The K value sets a minimum level for the amount of alumina needed--the smaller the K value, the further the fluoride concentration can be reduced;

(2) $^1/n$ is the differential increase needed in alumina concentration to reduce fluoride concentration levels, again the smaller $^1/n$ value* the less alumina needed to be added;

(3) $(^x/m)$ ultimate value is the loading capacity--the greater the $(^x/m)$ ultimate value the greater the amount (mg) of fluoride ion removed per gram of alumina used (this is the loading capacity).

* The larger $^1/n$ value, the more suited the alumina for column work since the alumina will have a higher reserve capacity taking into consideration that column work is to follow the isotherm studies indicates high $(^x/m)$ ultimate and $^1/n$ values plus low K value will give the most efficient fluoride removal. The overall ranking of the aluminas is as follows in Table IX.

TABLE IX

ALUMINA COMPARATIVE RANKINGS

Type Alumina	$^1/n$ Value	K Value*	$(^x/m)$ Ultimate	Overall
MCB Crushed Spheres (8 x 14 Mesh)	6th	6th	4th	6th
Kaiser A-300 Ungrd.	1st	1st	3rd	1st
Kaiser A-301 Spheres	2nd	4th	1st	2nd
ALCOA F-1 (28 x 48 Mesh)	4th	2nd	6th	4th
MCB Crushed Spheres (Crushed Finer)	5th	3rd	5th	5th
Kaiser A-301 Spheres (Crushed)	3rd	5th	2nd	3rd

* Contribution of K value felt to be 1/2 of value of $^1/n$ or $(^x/m)$ ultimate values.

Thus it is seen from Table IX that the Kaiser aluminas rank the highest in the important design parameter levels with ALCOA F-1, 4th, and MCB aluminas running last. Since Kaiser A-300 ungraded (a Kaiser experimental alumina) had not been released to the commercial market, it was decided not to use this material in future column tests. The Kaiser A-301 spheres (crushed) could not be accurately reproduced at RMA, and are not sold by Kaiser and therefore also had to be dropped. MCB's alumina both performed poorly and so were not considered for further column work. This left two aluminas, Kaiser A-301 Spheres and ALCOA F-1 (28 x 48 Mesh), to be tested in further column work at the Calgon plant.

CALGON PLANT ADSORBER EFFLUENT TREATMENT FOR FLUORIDE REMOVAL USING ALUMINAS SELECTED FROM ISOTHERM STUDIES

As mentioned in the previous section Kaiser A-301 Spheres and ALCOA F-1 aluminas were selected for column work at the Calgon plant to treat the adsorber effluent. It was also desired to test the effect of an aluminum sulphate presoak (reported to "activate" activated alumina) in increasing first cycle efficiency. Secondly, it was found desirable to test the regenerated alumina used by Ruebel and Hager, Inc., against their activated alumina. Accordingly, four 1 inch columns were set up in the Calgon plant with a common manifold connected in slip stream mode to the adsorber effluent port. The general layout of the test equipment configuration is given in Figure 13. The flow and column details are shown in Figure 14.

FIGURE 13

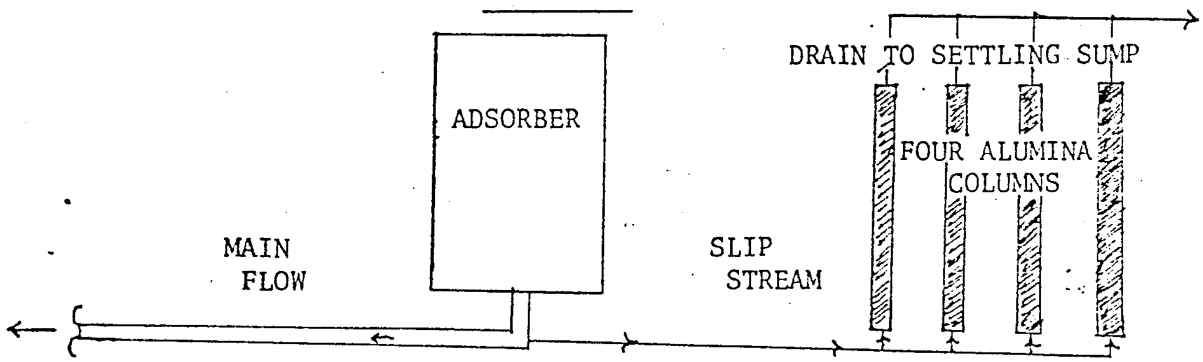


FIGURE 14

COLUMN AND FLOW DETAILS

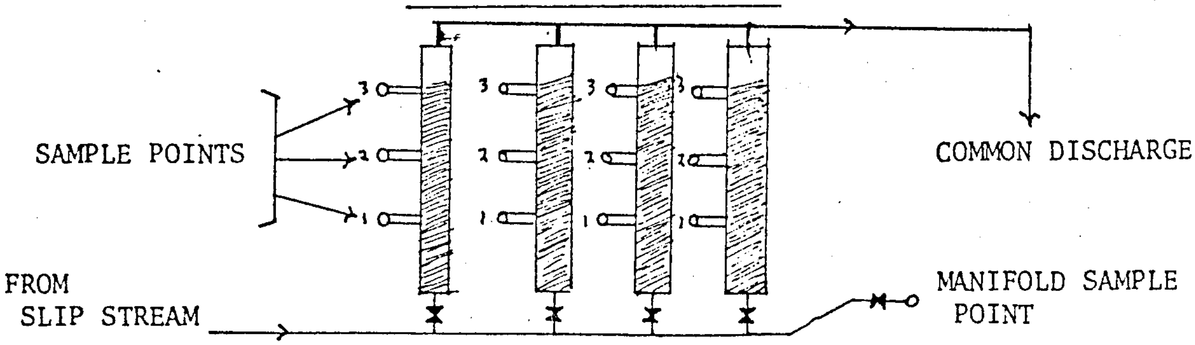


TABLE X

ALUMINAS USED IN EACH COLUMN

Column #1 - Kaiser A-301 Spheres (Untreated)

Column #2 - Kaiser A-301 Spheres (Aluminum Sulphate Presoak)

Column #3 - Regenerated ALCOA F-1 (28 X 48 Mesh)

Column #4 - Activated ALCOA F-1 (28 X 48 Mesh)

The aluminas were weighed (and in some cases preprocessed) and loaded into the columns in accordance with Table X above. The flow rates and time of flow rate start were begun and recorded. The flow rates were kept in the optimum range of 125-175 milliliters per minute with a 36 hour run performed. Water samples were collected at 4 hour intervals with half of the samples going to MALD for analysis and the other half of the samples being analyzed at the Calgon plant. TOC and pH values were taken from each 4 hour sample group to assure that each group was equivalent as to chemical loading with elapsed time (or total flow) the only difference between each sample group. The fluoride ion concentration levels for each sample group were tabulized for each column and sample point. The results are found in Table XI. Table XII gives the total flow thru the test alumina columns at the Calgon plant for each elapsed time period. A sample group is the block of samples taken at the end of a specified elapsed time. The chemical results of the tests for fluoride ion concentration levels were sent to SIAO for computer analysis using the Adsorption Column and Plotter Program. The results of this computer analysis is given in Figures 15, 16, 17 and 18 which follow. An examination of the figures mentioned results in certain conclusions. These conclusions are:

(1) A characteristic curve is formed by the plot of number bed volumes

versus fluoride ion concentration (a short drop to a valley followed by a fairly linear climb to a "saturation" plateau) for the Kaiser alumina columns except the aluminum sulphate presoaked column does not show as great a "short drop" phase,

(2) The ALCOA aluminas show a much improved fluoride ion removal performance over the Kaiser aluminas, and

(3) The regenerated ALCOA alumina is superior to the activated ALCOA alumina.

TABLE XI

FLUORIDE LEVELS VERSUS COLUMN SAMPLE POINT DURING TREATMENT OF CALGON PLANT EFFLUENT WITH ALUMINA COLUMNS

Sampling Group No.	Effluent	Fluoride Concentration ppm Column 1	Column 2	Column 3	Column 4	Sampling Point No.
1	4.15	3.0	2.05	.63	2.36	1
		1.9	1.28	.49	1.83	2
		1.51	.39	.47	1.77	3
2	4.20	1.80	1.28	.37	1.79	1
		1.19	.53	.34	1.53	2
		1.01	.33	.38	1.56	3
3	4.35	1.65	1.53	.70	2.07	1
		1.01	.66	.28	1.68	2
		.78	.41	.26	1.63	3
4.	3.80	3.55	3.55	.75	2.41	1
		2.41	2.36	.32	1.80	2
		1.58	1.61	.24	1.84	3
5.	3.4	3.15	3.3	.53	1.95	1
		2.15	2.30	.32	1.60	2
		1.65	1.95	.36	1.65	3
6	4.0	3.3	3.15	.485	2.15	1
		2.5	2.65	.345	1.65	2
		1.90	2.25	.225	1.65	3
7	3.5	3.25	3.25	1.15	2.4	1
		2.5	2.9	.50	1.85	2
		2.05	2.10	.43	1.80	3
8	3.5	3.15	3.3	1.25	2.4	1
		3.15	2.9	.80	2.3	2
		2.45	2.8	.85	2.05	3

TABLE XII

TOTAL FLOWS FOR EACH SAMPLE GROUP FOR THE ALUMINA COLUMN TEST AT CALGON PLANT

Sampling Group No.	Time	Elapsed Time (Mins.)	Column 1	Column 2	Column 3	Column 4
			Total Flows (ml)			
1	4 Oct 2035	260	6,750	7,250	17,800	43,730
2	5 Oct 0015	480	36,450	39,150	45,300	74,550
3	0530	795	78,975	84,825	84,675	118,650
4	0930	1035	108,975	114,825	121,875	146,250
5	1320	1265	137,725	143,575	157,525	172,700
6	1625	1450	160,225	166,700	186,200	193,975
7	2005	1670	188,825	196,400	214,800	228,075
8	6 Oct 0855	2441	230,675	252,200	303,150	348,975

Start: 1615 Hours 4 Oct 78
Stop : 0855 Hours 6 Oct 78

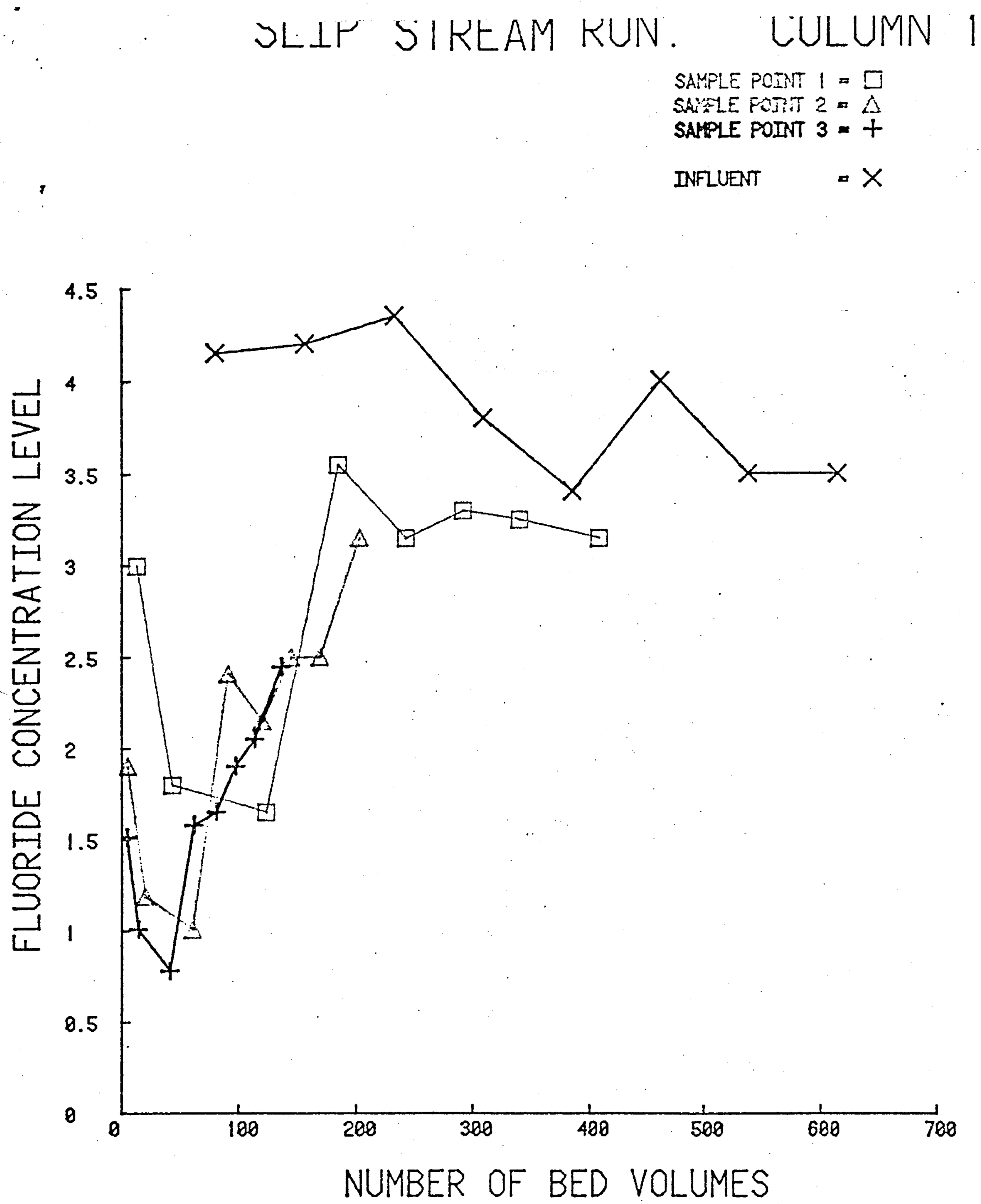

SLIP STREAM RUN. COLUMN 1
SAMPLE POINT 1 = □
SAMPLE POINT 2 = △
SAMPLE POINT 3 = +
INFLUENT = X
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
FLUORIDE CONCENTRATION LEVEL
0
100
200
300
400
500
600
700
NUMBER OF BED VOLUMES

FIGURE 15

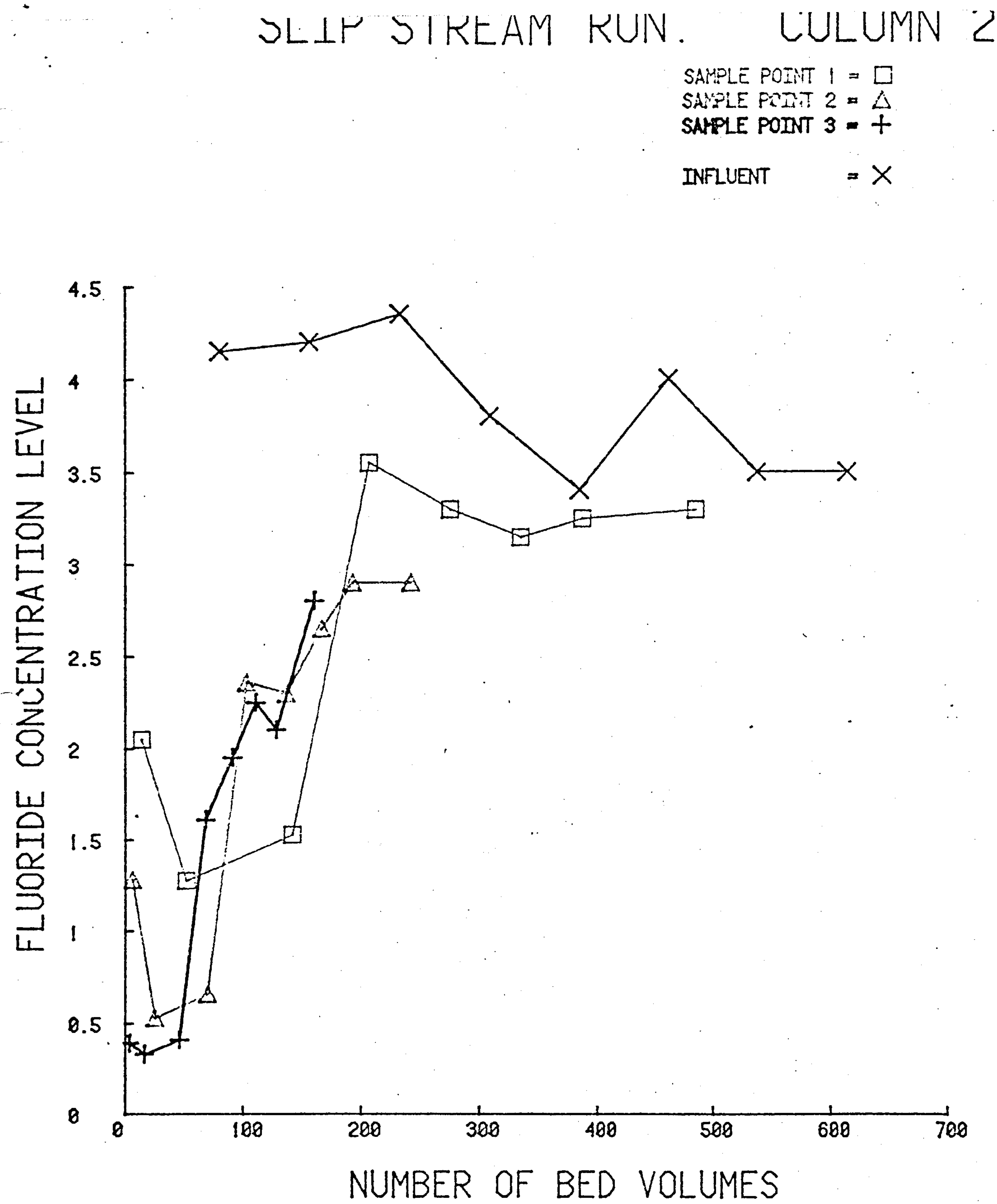

SLIP STREAM RUN. COLUMN 2
SAMPLE POINT 1 = □
SAMPLE POINT 2 = △
SAMPLE POINT 3 = +
INFLUENT = ×
FLUORIDE CONCENTRATION LEVEL
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
700
NUMBER OF BED VOLUMES

FIGURE 16

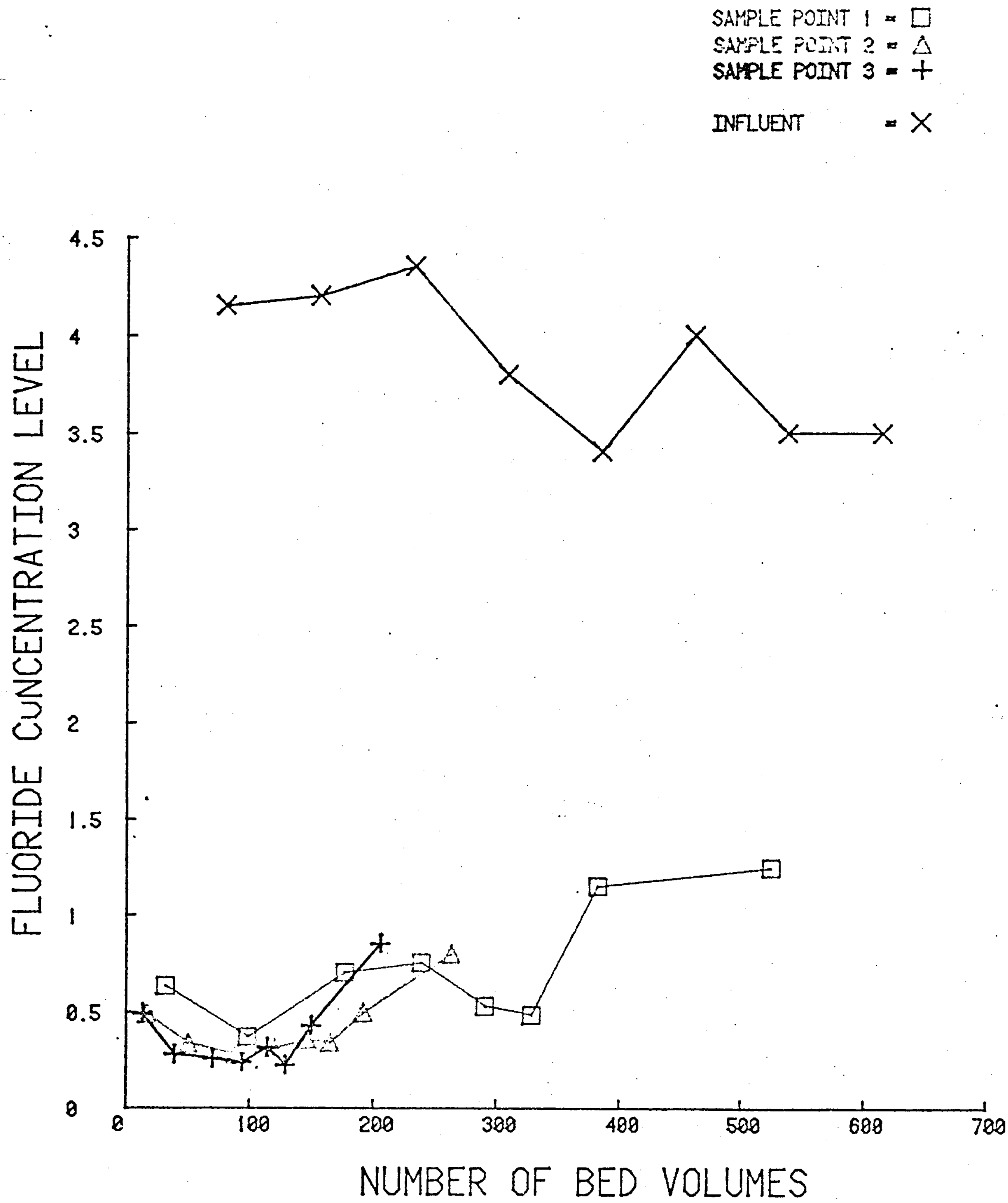

SAMPLE POINT 1 = □
SAMPLE POINT 2 = △
SAMPLE POINT 3 = +
INFLUENT = X
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
700
FLUORIDE CONCENTRATION LEVEL
NUMBER OF BED VOLUMES

FIGURE 17

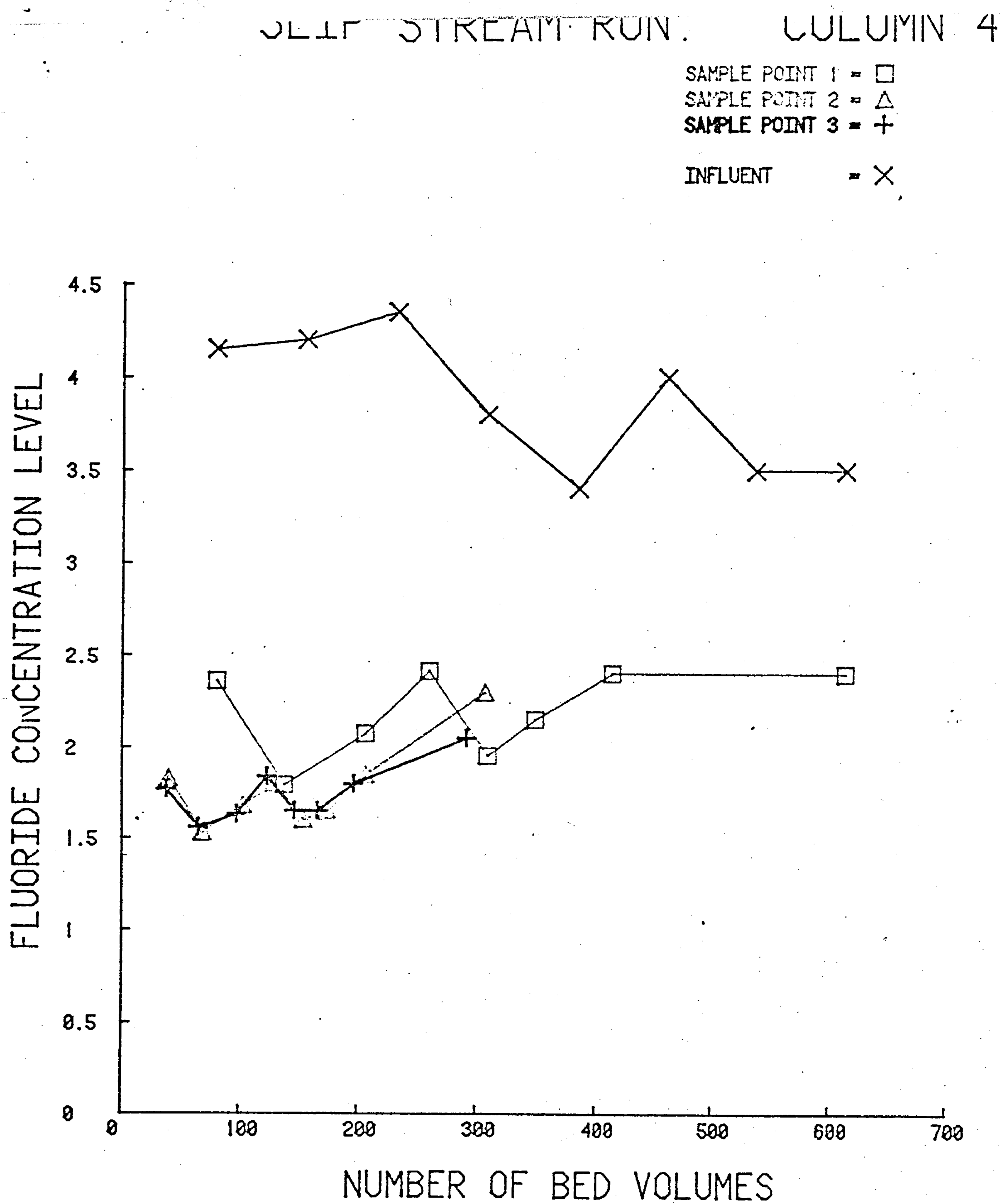

SLIP STREAM RUN. COLUMN 4
SAMPLE POINT 1 = □
SAMPLE POINT 2 = △
SAMPLE POINT 3 = +
INFLUENT = ×
FLUORIDE CONCENTRATION LEVEL
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
700
NUMBER OF BED VOLUMES

FIGURE 18

CONCLUSIONS AND RECOMMENDATIONS

Analysis of the data contained in this report leads to the following conclusions and recommendations:

(1) The statistical survey showed unacceptably high levels of fluoride ions at the North Boundary of Rocky Mountain Arsenal, thus generating a need for a fluoride ion removal process,

(2) The initial alumina columns showed an ability to significantly reduce fluoride ion concentration levels from activated carbon treated North Boundary water with isotherm tests required to "sort out" the best (highest loading capacity) alumina of those commercially available,

(3) The isotherm tests narrowed the field of commercial aluminas to two very promising candidates for column work verification,

(4) The work of Ruebel and Hager, Inc. established the feasibility and economic cost of an alumina column treatment system, and

(5) The column work at the Calgon plant while verifying which of the alumina selected from the isotherm tests also provided partial answers as to the type and treatment made of alumina for increases in fluoride ion removal efficiency.

This work, while addressing certain questions, pointed out what areas of the fluoride removal process which must be covered prior to construction of a fluoride removal system. The primary areas of concern are:

1. The disposal/treatment of regenerate sludge from the alumina column to prevent the creation of a contaminated basin.

2. A field scale plant test to set the engineering design parameters for an alumina adsorption column system to remove/reduce fluoride ion concentration levels to acceptable standards.

3. An update and transfer of modern fluoride removal technology to be accomplished through a literature review/research and bench studies with the P.M.O. receiving the final results.

4. A Quality Control plan to provide verification of field and full scale fluoride removal systems performance.

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